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Application of Membrane Technology to Power Generation Waters

Tennessee Valley Authority, Chattanooga

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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Application of Membrane Technology to Power Generation Waters

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PREFACE

The scope of this study has changed since its inception. Because electrodialysis removes only a small fraction of the impurities per pass, an early decision was made to focus on reverse osmosis and ultrafiltration. Pilot reverse osmosis and ultrafiltration modules were purchased and tested on various waste streams. For the most part, these tests were successful, and results were close to those that would have been predicted by the equipment vendors. Problems that occurred were generally related to pretreatment.

As conceptual design of reverse osmosis systems for application to power plant waters began, it became evident that pretreatment and reject stream disposal were often the largest part of the problem. Pretreatment such as pH and redox control, softening, and suspended solids removal can often produce water which is suitable for reuse, even though it may not meet water quality standards for discharge. Furthermore, concentrate disposal under zero discharge conditions can become expensive since an evaporator and storage ponds are generally required. Given the problem of reject disposal and using more modest product water quality requirements based on reuse, electrodialysis began to look more attractive. Electrodialysis is capable of producing a highly concentrated reject stream (up to 25-percent solids), thus eliminating the need for evaporators.

Alternatives to reverse osmosis treatments, including electrodialysis and the various technologies normally associated with reverse osmosis pretreatment, were included in a broader project scope. Because of limited resources, it was necessary to limit its depth, particularly in relation to alternative treatments. These options may be more deeply explored in subsequent studies.

ABSTRACT

Three membrane technologies (reverse osmosis, ultrafiltration, and electrodialysis) for wastewater treatment and reuse at electric generating power plants were examined. Recirculating condenser water, ash sluice water, coal pile drainage, boiler blowdown and makeup treatment wastes, chemical cleaning wastes, wet SO_2 scrubber wastes, and miscellaneous wastes were studied. In addition, membrane separation of toxic substances in wastewater was also addressed. Waste characteristics, applicable regulations, feasible membrane processes, and cost information were analyzed for each waste stream. A users' guide to reverse osmosis was developed and is provided in an appendix.

Treatment of power plant waters with membrane technologies to attain total water reuse and zero effluent discharge is technically feasible. Membrane technologies are not suited to remove materials which are unstable and apt to precipitate as they are concentrated; however, they excell in separating materials which are not susceptible to conventional wastewater treatment (including many toxic pollutants and dissolved solids). Thus, membrane technologies complement rather than compete with conventional technologies. For dissolved solids control, membrane technologies are viable alternatives to distillation. Distillation is more expensive but requires less pretreatment than reverse osmosis or electrodialysis. Electrodialysis is estimated to be the cheapest but does not produce product water of comparable quality to either reverse osmosis or distillation. To encourage wide acceptance of membrane technologies, demonstrations are needed to develop more definitive information on costs and reliability.

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LIST OF CONVERSION FACTORS

	Customary Units	International System of Units, (SI)
Length	1 inch, (in)	= 2.54 x 10^{-2} meters (m)
	1 foot, (ft)	= 0.3048 m
	1 yard, (yd)	= 0.9144 m
Area	1 in^2	= 6.45 x 10^{-4} m^2
	1 ft^2	= 9.29 x 10^{-2} m^2
	1 yd^2	= 0.8361 m^2
	1 acre	= 4.047 x 10^3 m^2
	1 hectare, (ha)	= 1.0 x 10^4 m^2
Volume	1 gallon, (gal)	= 3.785 x 10^{-3} m^3
	1 yd^3	= 0.7646 m^3
	1 acre-ft	= 1.233 x 10^3 m^3
	1 liter, (ℓ)	= 1.0 x 10^{-3} m^3
Weight	1 ounce, (oz)	= 2.8 x 10^{-2} kilograms (kg)
	1 pound, (lb)	= 0.4536 kg
	1 gram	= 1.0 x 10^{-3} kg
Pressure	1 pound/in^2, (psi)	= 6.895 x 10^3 Newtons/m^2 (N/m^2)
	1 atmosphere, (atm)	= 1.013 x 10^5 N/m^2
	1 bar	= 1.000 x 10^5 N/m^2
Flow	1 gal/day, (gpd)	= 4.381 x 10^{-8} m^3/second (m^3/s)
	1 gal/min, (gpm)	= 6.3 x 10^{-5} m^3/s
Flux	1 gal/(ft^2·day)	= 4.716 x 10^{-7} m/s
	1 mℓ/(cm^2·day)	= 1.157 x 10^{-7} m/s
	1 cm/day	= 1.157 x 10^{-7} m/s
	1 ℓ/m^2·day)	= 1.157 x 10^{-8} m/s

SECTION 1

INTRODUCTION

The electric power industry, the largest industrial water user in the United States, is facing a great challenge--to achieve zero pollutant discharge in the near future. The most practical approach to meeting this goal is to reuse water within the power plant.

Of the many technologies applicable in treating water for reuse, the membrane technologies are exceptional in their ability to efficiently separate and concentrate solutes from water. However, these technologies are relatively new and often misunderstood. This report reviews the three leading membrane separation technologies, the regulations which may motivate their increased use, and the various power plant water uses to which membrane technologies may be applied. Where appropriate, membrane technologies have been compared to more conventional technologies in order to define those areas where membrane processes are most applicable.

SECTION 2

CONCLUSIONS

Reverse osmosis, electrodialysis and ultrafiltration are proven technologies. Nevertheless they are relatively new and rapidly changing technologies that must be used with caution if successful application is to be assured. In many cases the successful use of membrane technologies requires an unusual degree of finesse in the conventional processes required for pretreatment. Thus, membrane technologies do not typically supplant conventional technologies, but serve to complement them.

Membrane technologies are not suitable for removing materials which are unstable and likely to precipitate as they are concentrated. These materials will foul membranes and should be removed by conventional techniques if possible. Thus, it is inappropriate to consider membrane technology as a method for preventing scale deposition

With proper pretreatment, reverse osmosis and electrodialysis can be used to remove and concentrate dissolved salts from various streams. In this role, membrane technology must compete with distillation. Distillation is typically more expensive but requires less extensive pretreatment than reverse osmosis or electrodialysis. Electrodialysis is estimated to be least expensive but does not produce product water of comparable quality to either reverse osmosis or distillation.

In considering electrodialysis, reverse osmosis, or distillation for removing dissolved solids, the need for dissolved solids control should be critically examined. When the need is established, membrane technology should be considered as a viable alternative to distillation. Closed-loop systems to which this concept could be applied include cooling systems, ash sluice systems, and SO_2 scrubber systems.

When heavy metals cannot be satisfactorily removed by pH adjustment, precipitation, adsorption, and suspended solids removal, reverse osmosis should be considered as a polishing step. Brine may be recycled to the precipitation step. This concept may be applicable to coal pile drainage and chemical cleaning wastes.

Ultrafiltration has been proven competitive in treating oily wastes and as a pretreatment for reverse osmosis.

Ultrafiltration and reverse osmosis have been shown to be effective in treating various radioactive wastes.

While reverse osmosis systems design is not an exact science, certain classes of problems can be handled in a straightforward manner. This includes processing solutions of inorganic ions to concentrate or purify, providing that adequate pretreatment is available. Pilot testing of the pretreatment step is advisable, but pilot testing of the reverse osmosis system is not generally necessary. Exceptions include situations where adequate pretreatment is not practical and where organic solutes or weakly ionized species are important.

Reverse osmosis is an acceptable process for removing inorganic and organic priority pollutants. Electrodialysis is feasible for removing only inorganic priority pollutants. Ultrafiltration holds no promise for removing priority pollutants from wastewaters.

SECTION 3

RECOMMENDATIONS

The following recommendations for future work are proposed:

1. An expanded "user's guide" is needed to acquaint potential users of membrane processes with the technology, to eliminate myths associated with membrane systems, and to encourage the application of membrane technology to water reuse in power plant operation.

2. Large-scale demonstrations are needed of both electrodialysis and reverse osmosis for controlling total dissolved solids in cooling water. This would provide the operating experience and cost data necessary for acceptance of these concepts by the power industry. Preliminary pilot studies and proper attention to conservative design should assure successful demonstrations.

3. Much work needs to be done in characterizing radwastes to determine their physical form. Decontamination factors for ultrafiltration and reverse osmosis modules need to be better established. The use of ultrafiltration to prevent fouling of ion exchange resins in nuclear plant water systems needs to be investigated.

4. Pilot plant work is needed to demonstrate the feasibility of boric acid and lithium-7 recovery from pressurized water reactor coolant using electrodialysis.

5. Further studies are recommended to perfect techniques for removing metals from coal pile drainage and chemical cleaning wastes. These studies might consider reverse osmosis as a polishing step.

6. If the technologies of brine concentration by reverse osmosis and electrodialysis are demonstrated as recommended for cooling water, experience from that study may be transferable to other closed loops such as ash sluice and SO_2 scrubber systems. Meanwhile, both of these systems need to be examined thoroughly through the use of parametric testing.

SECTION 4

MEMBRANE SEPARATION TECHNOLOGIES

The three major membrane separation processes for water and wastewater treatment are reverse osmosis, ultrafiltration, and electrodialysis. Each of these processes separates the feedwater into a concentrated stream and a depleted (purified) stream. Schematic diagrams of these processes are shown in Figure 1. Thermodynamically, each process has to overcome the free energy of mixing and may be compared to competitive processes on the basis of cost and energy efficiency.

A membrane separation system is based on the selective transport of species through a semipermeable membrane. The ability of some membranes to selectively pass certain species can be understood by assuming that species passing through the membrane must first dissolve in the membrane and then diffuse through it. The structure of the membrane then determines the relative ease with which various species dissolve in and pass through the membrane.

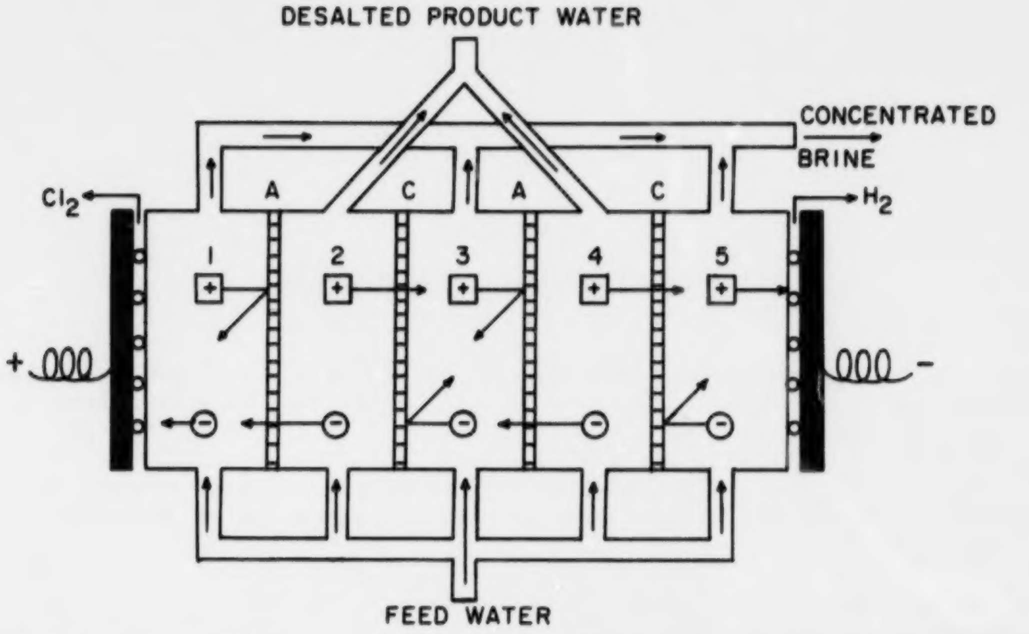
The selectivity of some membranes (typically the more open or porous materials) seems to be based primarily on solute size. Where this is the case, it may be assumed the mechanism is primarily that of a molecular sieve, controlled by the relative size and shape of the pores as compared to the size and shape of the solute molecules. This can be thought of as a special case of the solution-diffusion model where the chemical process of dissolution becomes relatively unimportant compared to the physical process of diffusion.

The driving force for transport through the membrane can be pressure, concentration, or electrical gradients. Table 1 shows a list of membrane separation processes, their functions, and the principal driving forces.[1]

REVERSE OSMOSIS

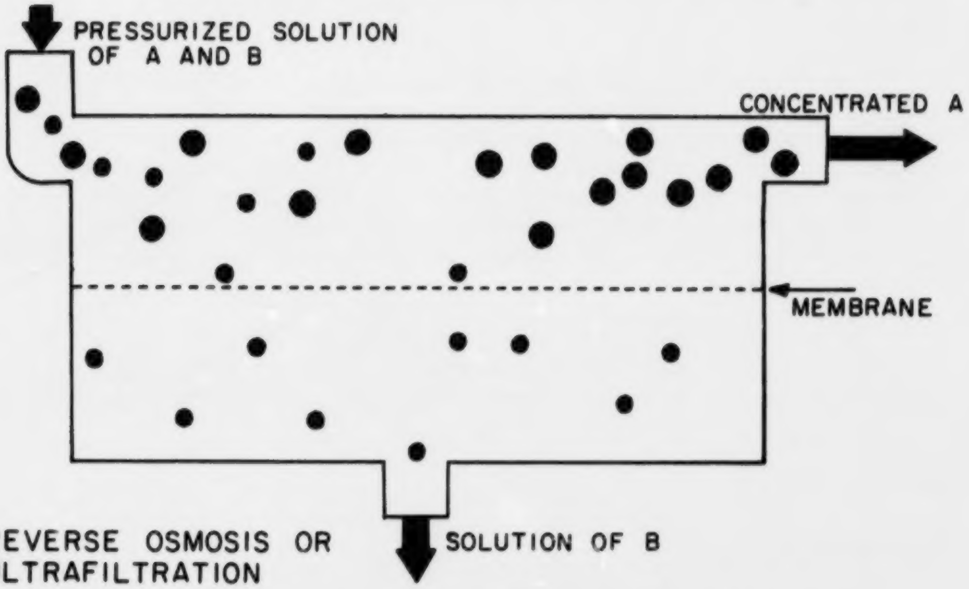
Fundamentals

Osmosis is a phenomenon that occurs between two solutions of different concentrations that are separated by a semipermeable membrane, through which water flows spontaneously from the less concentrated to the more concentrated solution. When a certain pressure is applied to the side of the more concentrated solution, the direction of water flow is reversed; that is, the water flows from the more concentrated to the less concentrated solution. This process is called "reverse osmosis." In the literature, it is also called "hyperfiltration." Reverse osmosis is a comparatively


DESALTED PRODUCT WATER
CONCENTRATED BRINE
Cl_2
H_2
A
C
A
C
1
2
3
4
5
+
-
FEED WATER

ELECTRODIALYSIS

A = ANION-PERMEABLE MEMBRANE
C=CATION-PERMEABLE MEMBRANE


PRESSURIZED SOLUTION OF A AND B
CONCENTRATED A
MEMBRANE
SOLUTION OF B

REVERSE OSMOSIS OR
ULTRAFILTRATION

Figure 1. Schematic diagram of membrane separation processes.

Source: Lacey, R. E. Membrane Separation Processes. Chemical Engineering. September 4, 1972, pp. 56-57. Reprinted by permission of the publisher.

TABLE 1. MEMBRANE SEPARATION PROCESSES AND PRINCIPAL DRIVING FORCES

Process	Function of membrane	Principal driving force
Reverse osmosis	Selective transport of water	Pressure
Ultrafiltration	Discriminates on the basis of molecular size, shape, and flexibility	Pressure
Electrodialysis	Selective ion transport	Electrical potential gradient
Dialysis	Selective solute transport	Concentration
Gel permeation chromatography	Retards high-molecular-weight solute penetration	Concentration
Liquid permeation	Selective transport of liquids	Concentration
Separation in a battery separator	Selective ion transport while retaining colloids	Electrical potential gradient
Oxygen determination by electrode	Control rate of depolarization	Partial pressure or concentration
Specific ion determination by electrode	Selective transport of an ion complex	Concentration (activity)

Source: Weber, W. J., Jr. Physicochemical Processes for Water Quality Control. Wiley-Interscience, 1972. p. 308. Printed by permission of the publisher.

new development for the separation, fractionation, or concentration of substances in an aqueous solution or gaseous mixture. Because no heat is added and no phase change is involved in product recovery, reverse osmosis is an effective process requiring relatively low energy input.

Reverse osmosis feedwater is pressurized by pumping and then channeled along the membrane surface. As product water (permeate) passes through the membrane, the feedwater becomes progressively more concentrated. A continuous flow must be maintained along the feedwater/concentrate side of the membrane to prevent an excessive buildup of dissolved solids. The concentrate stream leaving the system is often referred to as the "reject," especially in water purification applications.

The physical configuration must provide for distributing feedwater and collecting the concentrate and permeate. For membrane development work on a laboratory scale, the "plate and frame" arrangement is common. The frame supports a number of parallel sheets of membrane material and provides manifolds for distributing and collecting the water. Permeate compartments alternate with feed-concentrate compartments.

The most common configurations for commercially available membrane modules are tubular, spiral wound, and hollow fiber.

The tubular system typically uses porous or perforated tubes to support the membrane. Bundles of tubes are joined to a feedwater header system. Tubular devices enjoyed some degree of commercial success during the late

1960's. A number of vendors were successful in obtaining installations, especially in nonwater applications, such as chemical separations and food and drug processing. The tubular systems will handle larger particulate matter with less plugging than other designs, permitting feedwaters with low water quality to pass with a less stringent pretreatment requirement. Tubular units have a packing density of about 100 square feet* of membrane surface area per unit cubic foot of volume. This is an improvement over the plate and frame design, but the packing density of the tubular configuration is still considerably less than that of other configurations. Tubular units use a fluid velocity of 3 to 4 feet/second to maintain turbulence, thus preventing the buildup of dissolved salts at the membrane surface.

In the spiral-wound system, a large flat sheet of membrane is used to cover each side of a flat sheet of porous, water-conducting backing material. The membrane is sealed with adhesive on the two long edges and one end to form an "envelope." The other ends of the membrane are sealed to a perforated tube which receives the product water. A series of these envelopes are attached and wound around the central tube, separated from each other by a spacer. These spacers, typically an open-mesh material, provide a path for the feed-to-concentrate flow and are designed to promote turbulence. Packing density of this design is about 300 square feet of membrane per cubic foot of pressure vessel. Spiral-wound modules are more vulnerable to plugging from particulates in the feedwater than are tubular modules.

The hollow-fiber systems use hairlike capillary tubes of aromatic polyamide or cellulose triacetate membrane. Huge numbers of these microfibers, in a bundle configuration, have their ends potted in resin, which acts as a header to collect product water. A porous feed-distributor tube passes along the bundle axis, dead-ending just short of the tube sheet for the hollow fibers. Feed solution is introduced through this tube and passes radially outward through the fiber bundle, which is interspersed with cloth layers to maintain the bundle configuration and promote orderly flow. Product water passes inward through the fiber walls and is collected at the header. Concentrate is collected from around the periphery of the bundle.

Hollow-fiber systems have about 5,000 square feet of membrane surface per cubic foot of pressure vessel, by far the highest packing density of any membrane configuration. However, the flow per square foot of membrane area is lower than in other membrane systems. Hollow-fiber systems are more vulnerable to plugging from particulates in the feedwater than are tubular or spiral-wound systems.

Cellulose acetate membranes were the first to gain commercial acceptance; and there is now a variety of membranes based on cellulose acetate but with differing substructures, degrees of acetylation, and methods of fabrication. Noncellulosic membranes of commercial importance include aromatic polyamide (DuPont's B-9), poly-ether/amide (Universal Oil Product's PA-300), and laminated polyethylenimine cross-linked with toluene 2,4-diisocyanate (North Star's NS-100). Dynamically formed membranes of zirconium oxide and polyacrylic acid are also important but have not been packaged and marketed as modules since they may be formed during the operation itself.

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*For convenience, customary units are used in this report. To convert customary units to SI units, use the list of conversion factors given on page xii.

The appendix to this report entitled "A User's Guide to Reverse Osmosis" introduces the major factors which must be considered in specifying or buying reverse osmosis equipment. It focuses on the most readily available membranes, cellulose acetate and polyamide. For many industrial applications, however, high temperature membranes, such as the PA-300 or the dynamic membrane, should be considered. New membranes are being developed by several companies. Before applying new membrane materials, pilot testing is necessary to determine the effects on the membrane of various chemical and physical environments. Membrane lifetimes can only be determined after years of tests.

In choosing the operating pressure for a reverse osmosis system, tradeoffs must be considered between increased production at higher pressures and the resultant penalties of higher pumping cost and shorter membrane life. For brackish water desalting, pressures of 400 to 600 psi are common while pressures in the neighborhood of 600 to 1,200 psi are generally used for sea water.

Development

The osmotic phenomenon was known more than two centuries ago when Abbé Nollet's experiments on diffusion through animal membranes were published in 1748. Successful tests with artificially prepared membranes were performed by Traube in 1867.[2] About another century later, Reid, Breton, and others at the University of Florida under the sponsorship of the Department of the Interior studied desalinization with cellulose acetate membranes by using a trial-and-error approach to selecting the proper membranes for rejecting strong electrolytes. In the early 1950's, their work showed that the cellulose acetate membrane possessed characteristics of salt and water permeability that made it potentially attractive as a membrane for desalinization.[3,4] Loeb, Sourirajan, and others at the University of California followed up the research and developed a technique of casting a modified cellulose acetate membrane which gave water fluxes on the order of 10 to 20 gal/(ft^2·day), with salt rejections of 95 percent or better under a driving pressure of 600 to 800 psi. Development of this technique represented a significant advance in the technology and paved the way for the ultimate development of practical desalinization.[2,5] In the early 1960's, the Office of Saline Water supported several projects in research and development of reverse osmosis membranes, modules, and systems, which further advanced the technology for practical application.

In late 1962, Aerojet-General Corporation at Azusa, California, first studied the application of reverse osmosis to treating municipal wastewater. The bench-scale study was conducted on filtered, municipal, secondary effluent using 3-in.-diameter flat plate test cells and operating at pressures of 750 to 1500 psi. Results of the study showed that high-quality water could be produced from secondary effluent by reverse osmosis. In 1967, the Orange County Water District, California, operated a plate-and-frame reverse osmosis unit on a pilot scale for treating municipal wastewater.[6] Although they obtained results that corroborated the earlier study, plate-and-frame modules are no longer commercially available.

Spiral-wound and tubular membrane modules were pilot-tested by Gulf Environmental Systems Company (now the Fluid Systems Division of Universal Oil Products) in 1969 at Pomona, California. The tests on the Gulf spiral-wound modules indicated that the modules could process secondary effluent with high organic and inorganic removals, but some form of pretreatment or additional treatment of the secondary effluent was needed to prevent excessive clogging of the concentration-side spacers with suspended solids. Tests on the Universal Water Corporation tubular unit showed good removal efficiencies in more than 90 percent of the tests for all parameters except nitrate nitrogen, which was removed with 80.6 percent efficiency. Flushing the module for one hour with an 0.75 percent solution of "Biz" detergent increased the flux from 18.0 to 20.6 gal/(ft^2·day), compared with an original flux of 23.9 gal/(ft^2·day).[6]

In a laboratory study in 1969, Aerojet-General Corporation used conventional cellulose acetate membranes in flat plate cells and tubular configurations. Raw sewage, digester supernatant, and activated-carbon-treated secondary effluent from Orange County and Pomona sewage treatment plants were tested and found to exhibit very similar wastewater constituent rejections.[6]

In early 1970, the Gulf Environmental Systems Company modified the pilot spiral-wound reverse osmosis units to incorporate provisions for chemical and physical cleaning. The modified units were tested on five different feed streams: (1) primary effluent with and without sand filtration, (2) sand-filtered activated sludge effluent, (3) chemically clarified primary effluent with sand filtration, (4) chemically clarified primary effluent with sand filtration and activated carbon treatment, and (5) activated-carbon-treated activated sludge effluent. Results of these studies indicated that spiral-wound reverse osmosis units can be successfully operated on primary and activated sludge wastewater effluents with only moderate pretreatment and chemical cleaning. The activated carbon pretreatment is unnecessary on sand-filtered, activated sludge effluent or chemically clarified, sand-filtered, primary effluent.[6]

A pilot demonstration program was conducted by the Eastern Municipal Water District in Hemet, California, from March 6, 1970, to June 25, 1976, to determine the efficiencies and costs of pretreatment operations and to compare the performance of a selected group of reverse osmosis units manufactured by major firms. The pretreatment included (1) chemical clarification with alum in a sludge-blanket-type clarifier, (2) filtration in pressure units with single media, 0.45- to 0.55-mm sand, (3) granular carbon adsorption with 8 by 12 mesh carbon, (4) diatomaceous earth filtration in a 30-in.-diameter unit, and (5) chlorination with sodium hypochlorite. The reverse osmosis units tested included Aerojet-General Corporation's tubular unit, DuPont's hollow-fiber modules, Gulf's spiral-wound unit, Raypak's tubular unit, and Universal Water's tubular modules.

In these tests calcium deposits, organic slimes, and scaling were believed to be the mechanisms involved in membrane fouling.[6]

Pilot plant work at Lebanon, Ohio, from the late 1960's to the early 1970's tested different types of reverse osmosis units, including plate-and-frame, hollow-fiber, and tubular modules. Lime-clarified raw wastewater, secondary effluent, and primary effluent were treated. A tubular reverse osmosis unit can successfully treat municipal wastewater when membrane cleaning techniques are routinely practiced. When new membrane tubes were first used, flux decline took place, probably as a result of membrane compaction. The commercial bioenzyme Biz was found to be an effective chemical cleaner, and when primary effluent was treated, the insertion of turbulence promoters into each tube resulted in a 42 percent increase in flux.[6]

Application

Early development of reverse osmosis was directed toward seawater desalinization. In recent years, application of reverse osmosis has accelerated dramatically in both the depth of treatment technology and the breadth of application fields. Membranes of higher water flux and salt rejection under a lower driving pressure were developed for specific applications. Reverse osmosis is not only used for seawater and brackish water desalinization but also for domestic and industrial water and wastewater treatment applications. In municipal applications, reverse osmosis is used to remove total dissolved solids for potable water supply and to polish treated sewage effluents for reuse or ground water recharge. In industrial applications reverse osmosis is used for both process water purification and wastewater treatment, which in many cases can be consolidated into a single purpose, water reuse.

ULTRAFILTRATION

Fundamentals

Ultrafiltration is a membrane process that separates collodial materials and high-molecular-weight solutes such as proteins, soluble oil, microorganisms, polymers, clays, and natural gums from their solvent, usually water. Ultrafiltration is similar to reverse osmosis in being driven by pressure, using membranes made from similar materials, and operating in the same mode as far as the feed, permeate, and rejection streams are arranged. It differs from reverse osmosis in being unable to separate dissolved inorganic salts, using more porous membranes, and operating under lower pressure.

Because ultrafiltration is used to separate colloidal and high molecular weight materials, fouling of the membranes is often expected. To control fouling, both the membrane material and its physical configuration can be selected to facilitate cleaning.

Tubular configurations are generally used where fouling is expected to be severe. High fluid velocities and large diameter (up to one inch) tubes combine to create turbulence and scour the membrane walls. Tubular configurations also facilitate periodic mechanical cleaning and lend themselves to sponge ball cleaning systems similar to the Amertap system used for cleaning power plant condensers.

Spiral-wound ultrafiltration units are somewhat more vulnerable to fouling than tubular units. Where fouling of spiral-wound units can be controlled by chemical cleaning or flushing, they provide a significant savings over tubular units.

Hollow-fiber configurations are generally more vulnerable to fouling than the tubular- or spiral-wound configurations. To counteract this, one company (Romicon) has developed an ultrafiltration system using hollow fibers large enough to permit turbulent flow and rigid enough to permit backwashing.

Where fouling is expected, some method of chemical cleaning is usually planned in conjunction with mechanical cleaning, flushing, or backwashing. Pilot testing of the cleaning program is usually needed to establish efficacy and cost. When strong chemical agents are used, it is important to select a membrane material that will withstand repeated cleanings. Two membrane materials which can tolerate high temperatures and strong chemicals over a wide pH range are polysulfone and zirconium (IV) oxide. Other chemically resistant ultrafiltration membranes have been developed using proprietary materials.

Although susceptible to hydrolysis at high and low pH, cellulose acetate membranes are widely used for ultrafiltration. These membranes are produced in the same way as reverse osmosis membranes of cellulose acetate. Control of the annealing temperature is used to produce membranes of different porosities. Higher temperatures produce tight membranes with low water fluxes and high solute rejection.

Manufacturers sometimes specify the porosity of a membrane in terms of the "molecular weight cutoff," but this term tends to be misleading since solute passage is determined not only by a molecule's size but by its shape and charge distribution as well. This is illustrated by the poor rejection of organics exhibited by reverse osmosis membranes; small charged species are rejected while larger organics pass through. Nevertheless, in principal it is possible to establish a molecular weight cutoff for a given membrane by trying a wide variety of organic solutes. Typical molecular weight cutoffs range from 1,000 to 80,000. Membranes at the lower end of this range can exhibit some rejection of salts, blurring the distinction between reverse osmosis and ultrafiltration.

Pressures of 20 to 100 psi are typical for ultrafiltration systems; in contrast, reverse osmosis systems typically employ pressures from 400 to 1,200 psi.

Development

Application of ultrafiltration, or some processes similar to ultrafiltration, goes back to a distant past when pressurized filtration was practiced. Early workers used cellophane or porous cellulose nitrate membranes almost exclusively. Reproducibility was poor, and adsorption on pore walls and plugging were common.[1] The systematic study of the process and development of the membranes used did not start until investigation of reverse osmosis was under way. In the last few years, there has been a rapid development of the ultrafiltration process, especially in the area of industrial water and wastewater treatment.

Application

Ultrafiltration is suitable for applications in removing colloidal and high molecular weight organic solutes from water, especially for systems in which the high rejection of ionic and low molecular weight organic solutes is not required. Industrial applications in electroplating waste treatment, oil-water separation, chemical recovery from waste streams, food processing, and pharmaceutical waste treatment and water reuse have been successfully demonstrated. A recent study by Bhattacharyya et al.[7] demonstrated that ultrafiltration can be used to treat laundry and shower wastes with good solute removal at high water recovery, producing water suitable for nonpotable human contact uses.

ELECTRODIALYSIS

Fundamentals

Unlike reverse osmosis and ultrafiltration, which are pressure-driven, electrodialysis separation is induced by electric currents. Cation- and anion-selective membranes are alternately placed across the current path. The electrically attracted cations are allowed to pass through the cation membranes and the anions through the anion membranes, thus increasing and decreasing ionic concentrations in alternating spaces between the membranes. Reject streams, containing high concentrations of ions, and product streams, containing low concentrations of ions, can then be separated.

The active sites in ion-selective membranes are similar to those in ion-exchange resins. By making the polymer structure of the membrane sufficiently dense, passage of undesired ions and water is impeded while ions of the preferred charge diffuse through from one active site to another. A variety of membrane materials are now available. Desirable properties include physical strength, high selectivity, low electrical resistance, and resistance to chemical attack.

There are three different physical configurations commonly used for electrodialysis: the unit cell configuration and two plate-and-frame configurations, one using sheet flow and the other using a tortuous flow path. Each of these systems is described briefly as follows:

Unit cells are formed by sealing together anion and cation exchange membranes, making an envelope. A number of these envelopes are placed side by side in an array, separated by spacers which allow water to flow between envelopes. Electrodes are placed at each end of the array, and the entire assembly is contained in a tank provided with manifolds for feedwater distribution. Depleted water is collected in an overflow trough. Concentrated brine is produced within the unit cell envelopes and collected by way of small tubes which are sealed into the envelopes. This arrangement generates a very concentrated brine since water enters the brine cells only by diffusion through the membranes. The unit cell is less complex than the plate-and-frame configuration but suffers from poorer flow distribution. The cells cannot be disassembled to permit cleaning. If precipitation of dissolved salts occurs within a cell, it will swell and must be discarded.

Plate-and-frame configurations are engineered to provide more uniform flow conditions across the membrane but are inherently more complex. The frame holds a large number of parallel membranes pressed between gaskets to create a seal. Each compartment of the stack is provided with ports for water flow in and out, with alternate compartments manifolded together. The entire assembly can be dissassembled so that each membrane can be individually cleaned or replaced.

Sheet flow configurations use thin membranes which are closely spaced in order to minimize electrical resistance. Mesh or fabric spacers keep the membranes apart and provide for fairly even flow distribution in spite of the tendency for thin membranes to lose their shape.

To provide for greater turbulence and better control of flow patterns, the tortuous path configuration has been developed. In this system, flow along the membrane face is constrained to flow in a zig-zag pattern by a spacer which provides long thin flow channels. The high turbulence attained requires the use of thicker membranes and greater distances between them. The increased resistance attributable to greater distance is offset by the lessened resistance of the boundary layer. This is the layer of flow closest to the membrane, where turbulent eddies are inhibited by the membrane wall. These eddies enhance the diffusion of solute and reduce the electrical resistance of the solution.

Solutions can become depleted in the boundary layer when the diffusion of ions from the bulk solution does not meet the demand created by the flow of ions through the membrane. This usually occurs first at the anion membrane and results in the electrolysis of water. Current is then wasted in transporting OH$^-$ and H$^+$ ions. A key parameter in designing an electrodialysis system is the "limiting current density" at which water dissociation begins to occur. This is a function of the particular solute as well as the physical arrangement and flow rate.

Development

In 1903, Morse and Pierce introduced electrodes into the inner and outer chambers of a laboratory dialyzer and found that electrolytic impurities were more readily removed from gelatin when a voltage was applied. Schwein used electrodialysis in purifying sugar extracts around 1900. Later on, Pauli applied engineering design principles to reduce concentration polarization to a minimum in 1924. In 1940, Meyer and Strauss developed ion-selective membranes which were capable of operating against a concentration gradient with reasonable current efficiencies.[1] Substantial commercial development of electrodialysis systems started in the early 1960's, when the Office of Saline Water was strongly supporting a program for desalinization of brackish water, followed by the studies on wastewater application. From December 1962 through July 1963, secondary sewage effluent from the city of Clinton, Massachusetts, pretreated by cartridge filters and granular-activated carbon adsorption, was treated by two laboratory-scale electrodialysis stacks. Fouling of the membranes was detected, especially the anion membranes that absorbed organic materials, resulting in increased resistance and decreased capacity.[6,8]

In 1967, an electrodialysis pilot plant was tested in Orange County, California. The influent was municipal wastewater, with 15 to 20 percent industrial wastes treated by trickling filters, chemical filtration, dual-media filtration, and granular carbon sorption. The removal efficiencies were 22 to 30 percent for total dissolved solids. Membrane fouling was found to result primarily from the fraction of chemical oxygen demand represented by methylene-blue-active substances. It was concluded that if the feedwater were adequately pretreated the performance of an electrodialysis plant treating reclaimed water could be expected to parallel a similar plant treating brackish water of the same mineral content in terms of operating characteristics and costs.[6,9]

The Federal Water Pollution Control Administration operated a 60,000-gallons per day (gpd) electrodialysis pilot plant at Lebanon, Ohio in 1967 using municipal secondary effluent treated by diatomaceous filtration and granular carbon adsorption as the feedwater. A turbidity of less than 0.1 Jackson Turbidity Units (JTU), combined with periodic disinfection, was found to be the best way to control fouling. The membranes were not highly selective for any particular ion.[10]

In 1969, the Sanitation Districts of Los Angeles County operated a 15,000-gpd electrodialysis unit to treat municipal wastewater pretreated by activated sludge and granular carbon sorption. The pH in the concentrated stream was maintained at 3.5 by injection of sulfuric acid. Average reduction was about 34 percent for total dissolved solids, 15 percent for chemical oxygen demand, 43 percent for ammonia, 50 percent for nitrate, and 23 percent for phosphate. The membranes were cleaned every second day by flushing with an enzyme detergent, tap water, and acid.[6,11]

From March 1970 through June 1971, a 50,000-gpd electrodialysis pilot plant in Santee, California, treated municipal wastewater that had received activated sludge treatment followed by chemical clarification, dual-media filtration, and granular carbon adsorption. Removal efficiencies were 50 percent for total dissolved solids, 32 percent for chemical oxygen demand, 32 percent for nitrate-nitrogen, 22 percent for phosphate-phosphorus, 66 percent for calcium, and 68 percent for chloride. Flushing with acid, washing with enzymatic detergent, and injecting air were found to be helpful in mitigating fouling and increasing resistance. The deposit on the cation membranes was found to contain a higher proportion of inorganic matter than the deposit found on the anion membranes.[6]

Application

Electrodialysis has been actively used to desalt whey; to "sweeten" citrus juices; to desalt fishmeal wastewater; to recover chemicals such as carboxylic acid, pulping waste chemicals, and chromates; to denitrify agricultural runoff waters; and to desalt brackish water, which is by far the principal application. Its application in various salt removal or brine concentration processes such as cooling tower effluent reduction has also been demonstrated.[12] In Japan, the method of manufacturing salt has completely changed from the salt field method to the electrodialysis process since the end of 1971.[6] However, in the area of wastewater treatment, the profitability of the electrodialysis equipment has not been sufficient to support a large number of manufacturers and suppliers, as compared with reverse osmosis and ultrafiltration.

SIMILARITIES AND DIFFERENCES

Similarities

Reverse osmosis, ultrafiltration, and electrodialysis have several similarities:

1. Permeation of materials through semipermeable membranes achieves separation.
2. Feed, reject, and product streams are arranged in such a fashion that continuous operation is attainable.
3. There is no phase change.
4. No heat is needed for the separation process.
5. Boundary-layer effects or concentration polarization tend to occur.
6. Membrane fouling is possible.

Differences

There are several differences between reverse osmosis and ultrafiltration versus electrodialysis:

1. Reverse osmosis and ultrafiltration are driven by pressure, whereas electrodialysis is driven by electrical potential.
2. Reverse osmosis and ultrafiltration separate colloidal materials and high-molecular-weight solutes, whereas electrodialysis can only transfer ions, leaving colloidal and high-molecular-weight solutes in the diluted stream.

3. The power required for reverse osmosis and ultrafiltration is approximately proportional to the product water flow, but is not very sensitive to variations in the dissolved solids concentration of the feedwater. In contrast, the power required for electrodialysis is nearly proportional to the amount of salt removed but is only slightly sensitive to the flow rate.

4. Reverse osmosis and ultrafiltration can typically remove from 90 to 99 percent of the solute in one stage. Electrodialysis can typically remove from 25 to 60 percent per stage.

5. Electrodialysis can concentrate brine to between 10 and 25 percent solids (100,000 to 250,000 ppm) in one stage with feed solutions as low as 1,000 ppm. In contrast, ultrafiltration and reverse osmosis can concentrate feedwaters by a factor of less than 10 per stage and reverse osmosis is limited to a maximum concentration of approximately 70,000 ppm.

Contrasting reverse osmosis and ultrafiltration, reverse osmosis is designed to remove dissolved ions whereas ultrafiltration is designed to remove organics and particulates. Of course, reverse osmosis will remove many organics and particulates at the expense of fouling the membrane. To control fouling, ultrafiltration systems are generally designed for ease of cleaning by either mechanical or chemical means. Because of the more porous membranes used in ultrafiltration, typical pressures are between 20 and 100 psi. In contrast, typical reverse osmosis pressures range from 400 to 1,200 psi.

APPLICATIONS TO POWER GENERATION

Reverse Osmosis

Reverse osmosis is being used to produce high-quality boiler feedwater. When reverse osmosis is used as a pretreatment process ahead of mixed-bed ion exchange units, the demineralizers produce five to ten times more deionized water between regenerations; manpower requirements for operation and maintenance are reduced; and the reliability of water quality is improved. The chemical requirements are also lowered by 90 to 95 percent, and the life of ion exchange resins is extended,[13] which reduces costs and minimizes waste disposal problems. Raw water with a minimum concentration of total dissolved solids of 350 to 650 ppm is one criterion, in terms of costs, to justify using reverse osmosis as a pretreatment for deionization instead of a complete ion exchange system. However, if costs of wastewater treatment to meet the future stringent standards are considered, reverse osmosis application could be justified more easily.

Reverse osmosis has recently been applied in water and wastewater treatment at power plants. Applications included production of boiler feedwater, treatment of wastewater at steam plants, and treatment of liquid radwaste at nuclear plants.

In late 1971, Carolina Power and Light Company made provisions for the addition of a 53-gpm reverse osmosis system for radwaste application at the Brunswick Steam Electric Plant. This reverse osmosis system was provided to treat medium and low chemical priority wastewater associated with floor drains and demineralizer regeneration wastes.[14] The design of this system was based on pilot studies conducted at their H. B. Robinson Nuclear Plant.

A 250-gpm product capacity reverse osmosis system was operated at the Harrison Power Plant in 1972, mainly for supply of condensate makeup water. The station is jointly owned by the Potomac Edison Company, West Penn Power Company, and Monongahela Power Company. It was reported that the reverse osmosis unit offered advantages by reducing chemical operating cost and complexity of control and required less floor space than a multistep ion exchange system.[15]

A 2000-gpd prototype Westinghouse reverse osmosis unit was installed and operated at the Ginna Power Station of the Rochester Gas and Electric Company in 1972 to treat the plant's laundry waste. The reverse osmosis unit was capable of removing a minimum of 90 percent of the biological oxygen demand (BOD), phosphate, and radionuclides while reducing the waste volume ratio by a minimum of 100 to 1.[16]

A 200-gpm reverse osmosis system was installed in series with the existing 200-gpm makeup demineralizers at the Willow Glen Power Station of Gulf States Utilities Company in 1973. The advantages of reverse osmosis includes (1) lower overall operating costs, (2) greater overall capacity, (3) reduced manpower requirements, (4) removal of organic matter, (5) longer resin life, and (6) better quality effluent.[17]

In 1974, a 2500-gpm reverse osmosis (ROGA spiral-wound module) pilot plant was tested at the H Power Station of Karaso Electric Power Company in Japan to treat the power plant wastewater for reuse. Wastewater, electrostatic precipitator washing water, oily waste, and other continuous wastewater discharges were tested. It was concluded that the reverse osmosis process following the coagulation and filtration pretreatment was extremely reliable for power plant wastewater treatment.[18]

A 900-gpm, spiral-wound reverse osmosis system and other pretreatment processes were added upstream of a vapor-compression evaporator in 1976 at the San Juan Power Station owned jointly by Public Service Company of New Mexico and Tucson Gas and Electric Company. The reverse osmosis unit was selected to reduce the volume of waste going to the vapor-compression evaporator by a factor of five. The product waste from the reverse osmosis process was recycled for use as demineralizer input, as desulfurization-system makeup water, and in other station applications. This installation has reduced the normal cost of producing boiler makeup and has increased demineralizer-system capacity at little additional cost.[19]

A 75-gpm reverse osmosis unit was installed at North Lake Power Station of Dallas Power and Light Company in 1976 to produce boiler makeup water. It was reported that the installation was still free of significant problems after one year of operation.[17]

In 1977, a 400-gpm reverse osmosis system with cellulose-triacetate hollow-fiber membranes was placed in service at Coffeen Power Station of Central Illinois Public Service Company. The reverse osmosis unit was able to treat the lake water and to supply sufficient quality and quantity of boiler makeup water at the plant.[20]

When reverse osmosis is used to treat wastewater, the permeate is generally reused rather than discharged, because its quality is superior or comparable to available makeup water. Product water may be used for makeup to virtually any plant water system. This report considers the possible use of reverse osmosis to treat recirculating cooling water, ash sluice water, coal pile drainage, boiler blowdown, metal cleaning wastes, wet sulfur dioxide scrubber wastes, radioactive wastes, and oily and miscellaneous wastes.

Ultrafiltration

Floor washings from power plants that contain dilute concentrations of suspended solids, colloidal materials, oil, grease, and other constituents can be treated by ultrafiltration, after which the product water can be reused for ash transport water, additional floor washing requirements, and other applications. The resultant concentrate can be reduced in volume for ease of storage or disposal. Cooling tower blowdown can be treated with ultrafiltration, either alone or with reverse osmosis depending on the blowdown water quality. The high-quality water resulting from ultrafiltration plus reverse osmosis could be suitable for boiler feedwater, whereas the lower-quality water resulting from ultrafiltration alone can be used for washing operations. Boiler blowdown can also be treated with ultrafiltration, followed by reverse osmosis and ion exchange to provide product water for boiler feed.

A Romicon ultrafiltration pilot system was installed at the Ravenswood Power Station of Consolidated Edison Company to evaluate membrane flux and nonreactive silica rejection on untreated municipal water supply and deionized municipal water. The results showed that the ultrafiltration system was a very attractive pretreatment for boiler makeup demineralizers.[21]

At nuclear plants, ultrafiltration may be used to remove colloidal materials from radioactive waste streams. This would not only remove some of the radioactive materials but would also prevent fouling of ion-exchange resins or evaporators located downstream. Fouled resin is expensive to replace, and being radioactive it is also expensive to dispose. Fouled evaporators are difficult to maintain and have lower decontamination efficiency. This results in higher radiation doses to employees and to the downstream population.

Ultrafiltration of radioactive equipment drain wastes has been successfully demonstrated at the Tsuruga[22] generating plant (Japan). An EPRI sponsored program at the R. E. Ginna Nulcear Plant of Rochester Gas and Electric is now in progress to demonstrate the use of ultrafiltration as a pretreatment for radwaste evaporators.[14]

In summary, ultrafiltration can be used as a pretreatment to reverse osmosis for either water or wastewater treatment to produce high quality water for reuse, or it can be used alone for wastewater treatment to produce lower-quality water for suitable reuse purposes.

Electrodialysis

Electrodialysis has been shown to be applicable to cooling tower effluent reduction when it is used to remove and concentrate dissolved solids from a sidestream.[12] Similarly, electrodialysis may be applicable to the control of total dissolved solids in other recirculating waters such as ash sluice water.

Electrodialysis has been promoted for use in preparing boiler feedwater, but is at a disadvantage compared with reverse osmosis because it does not remove particulates and organics which foul ion exchange polishing resins. Also, several electrodialysis stages are necessary to produce water comparable with reverse osmosis permeate.

Separation of solute anions and cations can be accomplished in a special three-compartment electrodialysis stream. Feedwater enters the central compartment where the cations and anions begin moving toward their respective electrodes. At the cathode, hydroxides are formed by the electrolysis of water with hydrogen given off as a byproduct. The anode reaction forms hydrogen ions (H^+) giving off oxygen as a byproduct. A system of this type has been proposed for separating valuable lithium-7 from nuclear reactor waste streams.[23] The same concept[24] is also used in a proposed regenerable SO_2 scrubber system where the spent scrubber liquor, a solution of alkali and sulfate salts, is split into an alkali stream and a sulfuric acid stream. The alkali stream can then be reused in the scrubber. The sulfuric acid is recovered for other uses.

SECTION 5

REGULATIONS APPLICABLE TO POWER PLANT WATERS

The principal wastewaters from power generation are cooling waters, ash sluice waters, coal pile drainage, demineralizer regeneration wastes, boiler blowdown, metal cleaning wastes, sulfur dioxide scrubber wastes, radioactive wastewaters, and miscellaneous wastes such as oily wastes and floor drainage. In general, the characteristics of wastewaters vary with the types of plants and are governed by the sources and types of fuel used, plant configuration, process operation conditions, and feedwater quality.[25] In planning for pollution control, management must be cognizant of a wide variety of regulatory requirements applicable to these wastewaters and power plant discharges. These include regulations on discharges of dissolved and suspended materials as well as regulations on thermal discharges and releases of radioactivity. Thermal discharges are not considered in this study.

DISSOLVED AND SUSPENDED MATERIAL

Pursuant to the Federal Water Pollution Control Act of 1972 (PL 92-500), as amended by the Clean Water Act of 1977 (PL 95-217), and other Federal laws, and commonly referred to as the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) has established effluent limitations, guidelines, and new source performance standards for the point-source category of steam-electric power generating plants.[26] A summary of the applicable standards, set forth in 40 CFR part 423, is presented in Table 2. In general, limitations are set for free and total residual chlorine in cooling water discharges; for chromium, zinc, phosphorus, and other corrosion-inhibiting materials in cooling tower blowdown; and for suspended solids, oil, and grease in ash sluice water, boiler blowdown, metal cleaning wastes, and other low-volume wastewaters. Suspended solids are also limited in coal pile drainage and in effluents from construction activities. Concentrations of copper and iron are limited in boiler blowdown and metal cleaning wastes. In all sources, the pH is limited to the range of 6.0 to 9.0 (except once-through cooling water), and no polychlorinated biphenyls (PCB's) should be detectable. Through the National Pollutant Discharge Elimination System (NPDES) permit issuing program, these standards are applied.

The various state and local governments may have their own water quality and effluent standards for discharges, which are equal to or more stringent than those established by EPA.

TABLE 2. STEAM-ELECTRIC POWER GENERATING POINT SOURCE CATEGORY NONTHERMAL LIMITATIONS[a,b]

Waste Streams and Pollutants	Best Practicable Control Technology Currently Available (BCT)		Best Available Technology Economically Achievable (BAT)		New Source Performance Standards (NSPS)	
	max[c]	avg[d]	max[c]	avg[d]	max[c]	avg[d]
All waste streams						
pH (except once-through cooling)	6.0-9.0		6.0-9.0		6.0-9.0	
PCB's	No Discharge		No Discharge		No Discharge	
Low Volume Waste Streams						
T.S.S.	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ
Oil Grease	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ
Ash Transport Water						
T.S.S.	100 mg/ℓ	30 mg/ℓ				
Oil and Grease	20 mg/ℓ	15 mg/ℓ				
Bottom Ash Transport Water			e	e	f	f
T.S.S.			100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ
Oil and Grease			20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ
Fly Ash Transport Water						
T.S.S.			100 mg/ℓ	30 mg/ℓ	No Discharge	
Oil and Grease			20 mg/ℓ	15 mg/ℓ	No Discharge	
Metal Cleaning Wastes						
T.S.S.	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ
Oil and Grease	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ
Copper (Total)	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ
Iron (Total)	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ
Boiler Blowdown						
T.S.S.	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ	100 mg/ℓ	30 mg/ℓ
Oil and Grease	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ	20 mg/ℓ	15 mg/ℓ
Copper (Total)	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ
Iron (Total)	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ	1 mg/ℓ
Once-Through Cooling Water						
Free Available Chlorine[g]	0.5 mg/ℓ	0.2 mg/ℓ	0.5 mg/ℓ	0.2 mg/ℓ	0.5 mg/ℓ	0.2 mg/ℓ
Cooling Tower Blowdown						
Free Available Chlorine[g]	0.5 mg/ℓ	0.2 mg/ℓ	0.5 mg/ℓ	0.2 mg/ℓ	0.5 mg/ℓ	0.2 mg/ℓ
Zinc			1 mg/ℓ	1 mg/ℓ	No Discharge of Corrosion Inhibitors	
Chromium			0.2 mg/ℓ	0.2 mg/ℓ		
Phosphorus			5 mg/ℓ	5 mg/ℓ		
Other Corrosion Inhibitors			Case by Case Limit			
Area Run-off Subcategory[h]						
T.S.S.	≤50 mg/ℓ		≤50 mg/ℓ		≤50 mg/ℓ	
pH	6.0-9.0		6.0-9.0		6.0-9.0	
Pretreatment Standards[i]						
Free Available Chlorine	No Limitation		No Limitation		No Limitation	
Total Residual Chlorine	No Limitation		No Limitation		No Limitation	

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a. Except where specified otherwise, the allowable discharge equals flow multiplied by the concentration limitation. Where waste streams from various sources are combined for treatment or discharge, the quantity of each pollutant attributable to each waste source shall not exceed the specified limitation for that waste source.

b. All sources must meet State Water Quality Standards by 1977 [Section 301(b)(1)(c)].

c. Maximum for any one day.

d. Average of daily values for 30 consecutive days.

e. Allowable discharge equals flow multiplied by concentration divided by 12.5.

f. Allowable discharge equals flow multiplied by concentration divided by 20.0.

g. Limits given are maximum and average concentration.
Neither free available chlorine nor total residual chlorine may be discharged from any unit for more than 2 hours in one day and not more than one unit in any plant may discharge free available or total residual chlorine at any one unless the utility can demonstrate that the units in a particular location cannot operate at or below this level of chlorine.

h. Limits were remanded by the Fourth Circuit Court of Appeals in July 1976.

i. Applies only to sources which discharge to publicly owned treatment works. These discharges are also subject to the provisions of 40 CFR part 128.

Under Section 307 of the CWA, EPA was also required to publish effluent standards for toxic pollutants, with special attention to the 65 priority pollutants listed in Table 3. These, as well as other potentially toxic substances, are likely to be the focus of regulatory action in the future, and the power generation utility industry could shortly be faced with meeting potentially strict discharge limitations for the toxic pollutants found in its wastewater discharges. For instance, EPA has recently stated (45 Fed. Reg. 16,832) that:

> The Clean Water Act and a modified consent decree in NRDC v. Costle, 12 ERC 1833 (D.D.C. 1979), require that EPA develop guidelines to control toxic substances in industrial effluents. Section 307(a) of the Act identifies 65 toxic pollutants; they are listed in Table 1 of Committee Print 95-30 of the Committee on Public Works and Transportation, House of Representatives.
>
> Section 304 requires that EPA determine the best available technology (BAT) to control toxic pollutants from existing point sources. BAT will consist of the most effective technology which can still be economically achieved by the affected industries. EPA will also determine best conventional technology (BCT) which industries can use on conventional pollutants which do not require BAT.
>
> Under Section 306 of the Act, EPA is establishing new source performance standards (NSPS) for new plants. Under Sections 307(b) and 307(c), EPA will set pretreatment standards for both existing and new sources which discharge into municipal waste treatment systems. These sets of standards will in most cases require technologies equivalent to BAT.
>
> Major issues raised in setting effluent guidelines are:
>
> (1) Identification of the major pollutants discharged to and from treatment systems;
>
> (2) Determination of major technology options to control these pollutants;
>
> (3) Determination of the capital and annual costs of the technology options; and
>
> (4) Determination of the resulting economic impacts.

As a consequence, EPA is developing new guidelines for many industries, including the steam-electric power generating point-source category. Final modifications to 40 CFR part 423 are expected in December 1980.

Also, EPA is considering a major revision of water quality standards. This regulation may require states to adopt water quality standards for some toxic pollutants covered by ambient water quality criteria. One effect of this will be that dischargers (both municipal and industrial)

TABLE 3. LIST OF 65 TOXIC (PRIORITY) POLLUTANTS

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Aldrin/Dieldrin
5. Antimony and compounds*
6. Arsenic and compounds
7. Asbestos
8. Benzene
9. Benzidine
10. Beryllium and compounds
11. Cadmium and compounds
12. Carbon tetrachloride
13. Chlordane
14. Chlorinated benzenes
15. Chlorinated ethanes
16. Chloralkyl ethers
17. Chlorinated naphthalene
18. Chlorinated phenols
19. Chloroform
20. 2-chlorophenol
21. Chromium and compounds
22. Copper and compounds
23. Cyanides
24. DDT and metabolites
25. Dichlorobenzenes
26. Dichlorobenzidine
27. Dichlorcethylenes
28. 2,4-dichlorophenol
29. Dichloropropane and dichloropropene
30. 2,4-dimethylphenol
31. Dinitrotoluene
32. Diphenylhydrazine
33. Endosulfan and metabolites
34. Endrin and metabolites
35. Ethylbenzene
36. Fluoranthene
37. Haloethers
38. Halomethanes
39. Heptachlor and metabolites
40. Hexachlorobutadiene
41. Hexachlorocyclohexane
42. Hexachlorocyclopentadiene
43. Isophorene
44. Lead and compounds
45. Mercury compounds
46. Naphthalene
47. Nickel and compounds
48. Nitrobenzene
49. Nitrophenols
50. Nitrosamines
51. Pentachlorophenol
52. Phenol
53. Phthalate esters
54. Polychlorinated biphenyls
55. Polynuclear aromatic hydrocarbons
56. Selenium and compounds
57. Silver and compounds
58. 2,3,7,8-Tetrachlorodibenzo-p-dioxin
59. Tetrachloroethylene
60. Thallium and compounds
61. Toluene
62. Toxaphene
63. Trichloroethylene
64. Vinyl chloride
65. Zinc and compounds

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*The term "compounds" shall include organic and inorganic compounds.

may have to install treatment technology beyond that required by best practical wastewater treatment technology or best available technology (BAT) guidelines. A final rule is expected in May 1981.

In the same vein EPA is preparing additional quality criteria for toxics substances released into water. The states will refer to this guidance when they establish water quality standards. This guidance will be an important agency decision in the area of toxics. September 1980 is the anticipated date of its release.

Where toxics do pose a problem, membrane technologies can be used to recondition water for internal reuse. The reconditioned water may but need not necessarily meet discharge standards. Nevertheless, an assessment of membrane technology for treating wastewater streams for removal of toxic substances has been prepared and appears in Appendix B. The results of this assessment indicate the technical feasibility of removing priority pollutants from wastewater by membrane processes. Since water reuse is a national goal of high priority, the balance of this report shows how membrane technologies can assist in meeting this goal.

RADIOACTIVE WASTES

The release of radioactive wastes from nuclear power plants is regulated by the Nuclear Regulatory Commission (NRC). The Code of Federal Regulations, Title 10 Part 20, (10 CFR part 20) sets maximum concentrations of various radionuclides that will be permitted in the air and water outside of restricted areas. It also sets maximum dose rates to people both inside and outside restricted areas. At the same time, each nuclear plant must reduce radioactive releases below these levels to the extent practicable. This requirement is set forth in 10 CFR part 50 which requires that releases be "as low as is reasonably achievable" (ALARA). Appendix I of 10 CFR part 50 gives guidelines for determining ALARA compliance. The key requirement is that applicants shall "include in the radwaste system all items of reasonably demonstrated technology that, when added to the system, sequentially and in order of diminishing return, can, for a favorable cost-benefit ratio, effect reductions in dose to the population reasonably expected to be within 50 miles of the reactor." In calculating the benefits from dose reductions, a value of $1000/man-rem is to be used.

Several regulatory guides have been published by the NRC to aid in implementing Appendix I of 10 CFR part 50. United States Nuclear Regulatory Commission Reports[27,28] can be used to estimate releases. Dispersion in aquatic environments is estimated using Regulatory Guide 1.113.[29] Dose rates can then be calculated using Regulatory Guide 1.109.[30] Finally, the cost-benefit analysis is performed in accordance with Regulatory Guide 1.110.[31]

Since Regulatory Guide 1.110 deals only with "reasonably demonstrated technology" and includes reverse osmosis data from only one system (the laundry waste system at R. E. Ginna Nuclear Plant), designers who rely on this guide would be inhibited from innovative uses of membrane technology. The guide does not prohibit innovation but does recommend costs and decontamination factors that are to be used when determining the cost-benefit ratio for purposes of Appendix I of 10 CFR part 50. If other numbers are used, the burden of proof falls on the applicant.

SECTION 6

RECIRCULATING CONDENSER COOLING WATER

CHARACTERISTICS OF WASTEWATER

This discussion will not address once-through cooling systems, since the discharge from these systems is essentially natural surface water, altered only by the addition of chlorine or other biocides and occasionally by pH control within the range of 6 to 9.[32] Corrosion inhibitors are not generally used in once-through cooling water. With few exceptions, thermal effluent regulations now require recirculating cooling systems on all new power plants.

Cooling water quality is a function of the material flows in and out of the recirculating cooling water system. Sources of dissolved and suspended material include makeup water, chemical additives, air contaminates, and corrosion products. Outflows of dissolved and suspended materials include blowdown, droplets (drift) entrained in the cooling tower exhaust air and sludges and brines from various water treatment processes.

Sulfur dioxide and other chemicals as well as particulates are inadvertently scrubbed from the air in the cooling tower. By assuming an air analysis and 100-percent scrubbing efficiency, conservative estimates of this effect can be made. Similarly, by assuming a typical corrosion rate, the concentration of corrosion products, such as copper, zinc, and nickel, can be estimated.[33] Although these inadvertent sources are small in magnitude, they can result in significant concentrations in the recirculating cooling water system if blowdown flows are small.

Makeup water is generally the largest source of incoming dissolved and suspended solids. If the cooling systems water volume is to remain constant, makeup flows must equal the losses from evaporation, drift, and blowdown. Usually untreated surface water is used for makeup, although ground waters and treated wastewaters are sometimes used. Where available waters are extremely hard, makeup water is sometimes softened.

Management of cooling water chemistry is necessary to prevent the precipitation of scale on heat transfer surfaces. Potential scalants include calcium carbonate, calcium sulfate, calcium phosphate, and various magnesium and silica compounds. Typical operating limits for control of scaling are given in Table 4. Control methods include the use of softening, pH control, sequestering agents, and control of blowdown.

To prevent scaling from calcium, magnesium, or silica salts, softening may be applied to either the cooling tower makeup water or a small portion

TABLE 4. CONTROL LIMITS FOR RECIRCULATING WATERS

Constraint	Remarks
pH and hardness	
Langelier Saturation Index[a,b] $I_{sat} = pH - pH_s = 0.0$ to 1.0	pH = measured pH
Ryznar Stability Index[b] $I_{sat} = 2pH_s - pH = 6.0$ to 7.0	pH_s = pH at saturation with $CaCO_3$
Sulfate and calcium[c]	
$(C_{SO_4})(C_{Ca}) = 200{,}000$, where IS = 0.01	C_{SO_4} = concentration of SO_4 in mg/ℓ
$(C_{SO_4})(C_{Ca}) = 460{,}000$, where IS = 0.05	C_{Ca} = concentration of Ca in mg/ℓ
$(C_{SO_4})(C_{Ca}) = 730{,}000$, where IS = 0.1	IS = ionic strength
Magnesium and silica[d] $(C_{Mg})(C_{Si}) = 8{,}505$	C_{Mg} = concentration of Mg in mg/ℓ
$C_{SiO_2} = 150$	C_{SiO_2} = concentration of SiO_2 in mg/ℓ

[a] Chen, Y.S., J. L. Petrillo, and F. B. Kaylor "Optimal Water Reuse in Recirculating Cooling Water Systems for Steam-Electric Generating Systems." In Proceedings, Second National Conference on Complete Water Reuse, Chicago, Illinois, May 1975. Sponsored by American Institute of Chemical Engineers, New York. pp. 528-541.

[b] Ryznar, J. W. "A New Index for Determining Amount of Calcium Carbonate Scale Formed by a Water." Journal American Water Works Association, Vol. 36, No. 4, April 1944. pp. 472-486.

[c] Selmeczi, J. G. and J. P. Miller. "Supersaturation of Calcium Sulfate in Water." Paper presented at American Chemistry Society, Great Lakes Regional Meeting. Purdue University. West Lafayette, Indiana. June 4, 1974. 27 pp.

[d] Nelson, E. R. "Water Recycle/Reuse Possibilities: Power Plant Boiler and Cooling Systems." EPA-660/2-74-089. December 1974. 51 pp.

(sidestream) of the recirculating cooling water flow. Comparing makeup and sidestream softening, sidestream softening provides for the cooling system to preconcentrate the flow, thus permitting a smaller softening system. Nevertheless, where makeup waters are very high in hardness, makeup softening may be advantageous. At the site of the proposed Sundesert Nuclear Plant, using agricultural runoff as makeup, recent pilot plant tests showed that superior results can be obtained by combining the makeup with a sidestream before softening.[34]

Control of pH is helpful in preventing calcium carbonate scale and controlling corrosion. For control of carbonate scale acid is usually added to lower the alkalinity and to convert carbonate ions to bicarbonate. Sulfuric acid is usually used because of its low cost, but the increased threat of calcium sulfate scaling must be considered. Although maintaining a low pH helps control carbonate scale, too low a pH will result in increased corrosion and should be avoided. It is seldom necessary or advisable to reduce the pH below 7.

Some antiscaling agents act to distort the crystal structure of scale deposits, slowing their growth. Commonly used agents include polyphosphonates, polyacrylates, and natural organics. Sequestering agents such as sodium hexametaphoshate can combine with potential scalants to prevent their deposition. These treatments are generally designed to delay the deposition of scale, causing it to be soft, amorphous, and more easily removed should deposition occur. Additives of this type would presumably interfere with the operation of softening systems.

Typically, the major outflow of dissolved solids is through the blowdown. By increasing the makeup and blowdown flows, the concentration of all major ions can be reduced. This in turn reduces the potential for scale deposition. Other outflows of both water and dissolved solids may occur as sludges or brines from various treatment schemes. With proper design, these flows may be adequate to maintain a mass balance without blowdown. It is clear that the total mass of dissolved solids leaving the system must (on an average) equal that entering. Thus, some provision must be made to remove this dissolved solids loading.

High concentrations of dissolved solids can lead to increased corrosion rates because high conductivity increases the rate of electrolytic corrosion and because high concentrations of particular ions can cause corrosion. Chlorides are particularly corrosive to stainless steels, and sulfates can create cracking in some concretes.

Corrosion control is sought through the use of chemical additives, pH control, sacrificial anodes, and corrosion resistant materials. Common additives are based on zinc, chromium and phosphate compounds.

Biocides are commonly used to control the growth of slime on heat transfer surfaces. Chlorine is the most widely used, but a number of proprietary biocides are also available.

ALTERNATIVE TREATMENTS

Reverse osmosis can be used to produce high quality water from cooling tower blowdown in a single stage and to produce a concentrated brine by using several stages. In this role, reverse osmosis is similar to evaporative brine concentrators. In contrast, electrodialysis requires several stages to produce high quality water, but only one stage to produce a highly concentrated brine. Because electrodialysis is capable of producing a more concentrated brine than reverse osmosis, brine disposal costs can be reduced. The primary purpose of each of these salt removal methods is to control the total dissolved solids concentration in the cooling system and to avoid corrosion.

Conventional blowdown will serve the same purpose if it can be discharged. Conventional methods of treating blowdown for discharge should be considered. These include pH control and aeration to precipitate metals and the use of higher blowdown rates to reduce their concentration. Coagulation, settling, and filtration can be used for suspended solids removal. (Ultrafiltration is not cost effective in this role.) Where conventional treatments fail to produce an acceptable discharge, water reuse must be considered.

One water reuse option is to allow sidestream softening sludge and cooling tower drift to serve as the only blowdown, resulting in very high concentrations of dissolved solids. Corrosion resistant materials can be used to reduce the need for controlling dissolved solids.

Electrodialysis

By treating a sidestream of the recirculating cooling water, electrodialysis can be used to maintain dissolved solids at a low level in the cooling system while producing a low volume of concentrated brine. Brine must generally be stored on site, although other disposal methods are sometimes available. Pretreatment by softening and filtration is necessary to prevent scaling of the membranes. The softening step also serves to prevent scaling within the cooling system.

According to Jordan et al.,[12] numerous case studies have shown that electrodialysis is less expensive than alternative systems for salt removal and concentration. A study by Blackburn[35] shows that at salt removal rates and concentration ranges applicable to power plant cooling towers, electrodialysis is one of the most cost-effective processes for salt removal. In fact, for waters with dissolved solids concentrations less than 10,000 ppm (one percent), his data shows electrodialysis to be much less expensive than evaporative brine concentrators.

In spite of this, vapor-compression distillation has been selected over electrodialysis for cooling water brine concentration at several recent plants designed for zero liquid discharge.[36] Apparently, the lack of experience with electrodialysis installations of this type has been an important factor. Utilities require reliable technologies with proven operability. Although electrodialysis has been used for desalting water supplies in many communities throughout the United States, large-scale use of electrodialysis to concentrate brine has been primarily limited to Japan, where it is used to concentrate salt from sea water.[37]

A large-scale demonstration of electrodialysis to remove salt from cooling water would be useful to answer questions about the reliability and cost of such systems in the United States. Design of a large-scale system can be accomplished after key parameters, such as cell resistance and limiting current density, are established in small-scale tests.

Reverse Osmosis

Reverse osmosis can be used to treat cooling water for discharge or for reuse. Because reverse osmosis permeate is generally of high quality, it would usually be reused. The brine, however, is more concentrated than the feed and often must be stored indefinitely or disposed at high cost. If this is the case, overall cost is reduced by concentrating the brine as much as possible, thus reducing its volume.[38]

Brine concentration by reverse osmosis is usually limited first by calcium sulfate deposition and then by osmotic pressure increases. To minimize the blowdown flow, cooling water will usually be concentrated to the maximum extent possible without the precipitation of scale. Whatever the potential scale forming species may be, further concentration in the reverse osmosis process will lead to scaling of the membranes unless precautions are taken. Typically, softening would be used to prevent calcium and magnesium scaling. Scale inhibiting chemicals may also be used. Otherwise, water recovery must be limited to ensure that solubility limits are not exceeded in the brine.

Osmotic pressure also limits water recovery. System pressure must substantially exceed the osmotic pressure in order to maintain practical premeate productivity rates. Reverse osmosis modules designed for brackish water desalting are limited to operating pressures below 400 to 600 psi depending on the module; and practical brine concentrations are in the neighborhood of 15,000 to 20,000 ppm. Higher concentrations, up to about 70,000 ppm, are feasible in modules designed for sea water desalting.

Cooling water is, for the most part, concentrated natural waters, and there is a large data base on the treatment of natural waters. Nevertheless, treatment of cooling water is different in that chemicals may have been added to reduce scaling or corrosion and corrosion products may be present. Also, the problem of brine concentration and disposal is more significant.

Reverse osmosis has been proven to be applicable in treating cooling water for reuse.[39,33]

Chian and Fang's study[40] indicated that cellulose acetate and aromatic polyamide membranes satisfactorily removed chemicals from cooling tower blowdown. At 67 percent product recovery, permeates from both membranes contained a smaller amount of chemicals than those found in municipal water used for the makeup feedwater. A higher product water recovery should be used in practice to an extent limited only by the solubility of calcium sulfate.

TVA conducted a preliminary study on treating cooling tower blowdown by reverse osmosis. One blowdown sample obtained from a steam plant in the southwest was filtered through 1- to 3-μm fiber filters for suspended solids removal, and then the blowdown was tested by four reverse osmosis modules: DuPont Spiral-Wound Polyamide membrane, Dow Hollow-Fiber Cellulose Triacetate membrane, Roga Spiral-Wound Cellulose Triacetate membrane, and DuPont Hollow-Fiber Polyamide membrane. The testing results based on 10 percent volume recovery are shown in Table 5 and indicate a high percentage removal of chromium, zinc, and phosphate, commonly used corrosion inhibitors.

Kasarek[39] proposed a calcium reduction system in addition to the reverse osmosis system to facilitate further water recovery. The reverse osmosis system consists of a holding pond to equalize the flow and to cool the tower blowdown; a blend tank to control temperature and pH and to feed antiscalent; a cartridge filter; and the reverse osmosis units. The calcium reduction system consists of a chemical feed to inhibit and counteract the antiscalent in the reject stream and cause the calcium sulfate to precipitate. After clarification, the sludge is blown down, and the supernatant is pumped back to the blend tank for further water recovery. The sludge can be dried in an evaporation pond to achieve a complete zero discharge. For a water production rate of 144,000 gpd at a feed recovery of 80 percent, the capital cost was estimated to be $200,000 in 1977. The operating and maintenance cost was $2.05 per thousand gallons of product water, assuming $3.00 per thousand pounds of steam, $0.04 per thousand gallons of cooling water, and $0.02 per kWh of electricity. Including the capital investment, with an interest rate of 10 percent and 1 percent of investment as taxes, the total yearly cost of the system was $2.47 per thousand gallons of product water.

Overall costs of a brine concentration/water purification system should include the costs of ultimate brine disposal as well as credits for high quality water produced for reuse. Where waste brine must be stored on site or evaporated, costs are reduced when volume reduction by reverse osmosis is increased to its practical limits. A study by Dow[38] illustrates the advantages of high recovery when ponding or deep well injection is used for brine disposal. Compared to the vapor-compression evaporative brine concentration process, reverse osmosis is less costly in both capital and operating cost. Reverse osmosis power requirements range from 10 to 30 kWh per thousand gallons while vapor compression evaporation requires from 70 to 90 kWh per thousand gallons. In terms of 1976 dollars, operating and maintenance costs of reverse osmosis and vapor-compression evaporators are estimated at 45 to 50 cents per thousand gallons and $2.35 per thousand gallons respectively. Equipment and installation costs are estimated at $.90 per gallon per day for reverse osmosis and $7 per gallon per day for evaporators. (These figures are based on estimates made for TVA by Sheppard T. Powell Associates.)

At the San Juan generating station,[19] the Public Service Company of New Mexico found the use of reverse osmosis more economical than evaporators alone. Reverse osmosis is being used to preconcentrate cooling tower blowdown prior to treatment by a vapor-compression evaporative brine concentrator. The reverse osmosis system is designed to concentrate the blowdown by a factor of five, reducing the required evaporator

TABLE 5. RESULTS OF REVERSE OSMOSIS STUDIES ON COOLING TOWER BLOWDOWN TREATMENT

Membrane type[a]	Feed composition	Permeate (gal/min)	Rejection (%)	Operation Pressure (psig)
DuPont Spiral Wound	Alkalinity (total), 58.1 mg/ℓ as $CaCO_3$	0.45	84.3	400
	Conductivity, 4700 µmho	0.45	82.1	400
	TDS, 4000 mg/ℓ	0.45	85.8	400
	COD, 24 mg/ℓ	0.45	95.8	400
	Cr, 0.01 mg/ℓ	0.45	>80	400
	Zn, 0.2 mg/ℓ	0.45	85	400
	PO_4-P (total), 0.49 mg/ℓ	0.45	93.9	400
	Kjeldahl-N, 0.95 mg/ℓ	0.45	78.9	400
	$(NO_2 + NO_3)$-N, 17 mg/ℓ	0.45	80	400
	pH, 6.3 units	0.45	-	400
Dow Hollow Fiber[b]	Alkalinity (total), 43 mg/ℓ as $CaCO_3$	0.27	90.7	200
	Conductivity, 5000 µmho	0.27	95.6	200
	TDS, 4300 mg/ℓ	0.27	95.3	200
	COD, 19 mg/ℓ	0.27	89.5	200
	Cr, 0.01 mg/ℓ	0.27	>80	200
	Zn, 0.25 mg/ℓ	0.27	92	200
	PO_4-P (total), 0.67 mg/ℓ	0.27	98.5	200
	Kjeldahl-N, 0.78 mg/ℓ	0.27	48.7	200
	$(NO_2 + NO_3)$-N, 18 mg/ℓ	0.27	87.2	200
	pH, 6.3 units	0.27	-	200

TABLE 5 (continued)

Membrane type[a]	Feed composition	Permeate (gal/min)	Rejection (%)	Operation Pressure (psig)
Roga Spiral Wound	Alkalinity (total), 70 mg/ℓ as $CaCO_3$	1.1	91.4	400
	Conductivity, 4100 µmho	1.1	85.2	400
	TDS, 8300 mg/ℓ	1.1	80.7	400
	COD, 21 mg/ℓ	1.1	33.3	400
	Cr, 0.01 mg/ℓ	1.1	>80	400
	Zn, 0.37 mg/ℓ	1.1	83.8	400
	PO_4-P (total), 1.34 mg/ℓ	1.1	96.3	400
	Kjeldahl-N, 0.45 mg/ℓ	1.1	71.1	400
	$(NO_2 + NO_3)$-N, 27 mg/ℓ	1.1	64.8	400
	pH, 6.5 units	1.1	-	400
DuPont Hollow Fiber	Alkalinity (total), 72 mg/ℓ as $CaCO_3$	1.6	86.5	400
	Conductivity, 8900 µmho	1.6	89.2	400
	TDS, ---	1.6	-	400
	COD, 35 mg/ℓ	1.6	94.3	400
	Cr, 0.01 mg/ℓ	1.6	>80	400
	Zn, 0.89 mg/ℓ	1.6	96.6	400
	PO_4-P (total), 1.74 mg/ℓ	1.6	97.1	400
	Kjeldahl-N, 0.55 mg/ℓ	1.6	87.3	400
	$(NO_2 + NO_3)$-N, 55 mg/ℓ	1.6	84.5	400
	pH, 6.4 units	1.6	-	400

[a] Feedflow rate for all modules was 4 gal/min.
[b] The Dow module was a low pressure module designed for testing purposes.

size by a similar factor. Operating costs for the reverse osmosis system are about \$1.00 to \$1.20 per thousand gallons of treated water. Considering the combination of reverse osmosis and evaporation together, the operating cost is estimated at \$1.70 to \$1.80 per thousand gallons.

To enhance user confidence in reverse osmosis, a User's Guide to Reverse Osmosis has been included as an appendix to this report. Most of the problems reported with reverse osmosis systems in the past have been caused by poor pretreatment and design, but are not inherent to the technology. The appendix discusses the major factors which must be considered in specifying or buying a reverse osmosis system with special attention to potential problem areas.

In selecting a reverse osmosis system for treating cooling water, the temperature tolerance of the membranes should be carefully checked against expected water temperatures. Some type of auxiliary cooling may be necessary as pretreatment to the reverse osmosis unit. Other pretreatment needs are discussed in the appendix.

RECOMMENDATIONS

When a cooling system is required to operate with zero liquid discharge and dissolved solids must be controlled, electrodialysis is apparently the most cost-effective approach to removing and concentrating dissolved solids for storage. The recommended system would treat a sidestream of the recirculating cooling water. Softening and filtration would precede electrodialysis. The electrodialysis unit would produce a salt-depleted stream which would be returned to the cooling system and a concentrated stream which would be stored in lined ponds.

A combination of reverse osmosis and evaporative brine concentration can be used instead of electrodialysis. Using reverse osmosis serves to preconcentrate the brine and substantially reduce the cost of the evaporation step. This system may be superior to electrodialysis where large volumes of permeate or distillate quality water are needed in other plant systems.

Flow diagrams of the recommended systems are shown in Figures 2 and 3. Note that hot water feed is preferred for electrodialysis because it improves performance, while cool water is often desirable for reverse osmosis in order to prevent membrane hydrolysis.

Large-scale demonstrations of these concepts are recommended to provide cost data and demonstrate operability. Of the two systems, electrodialysis appears to offer the most promise.

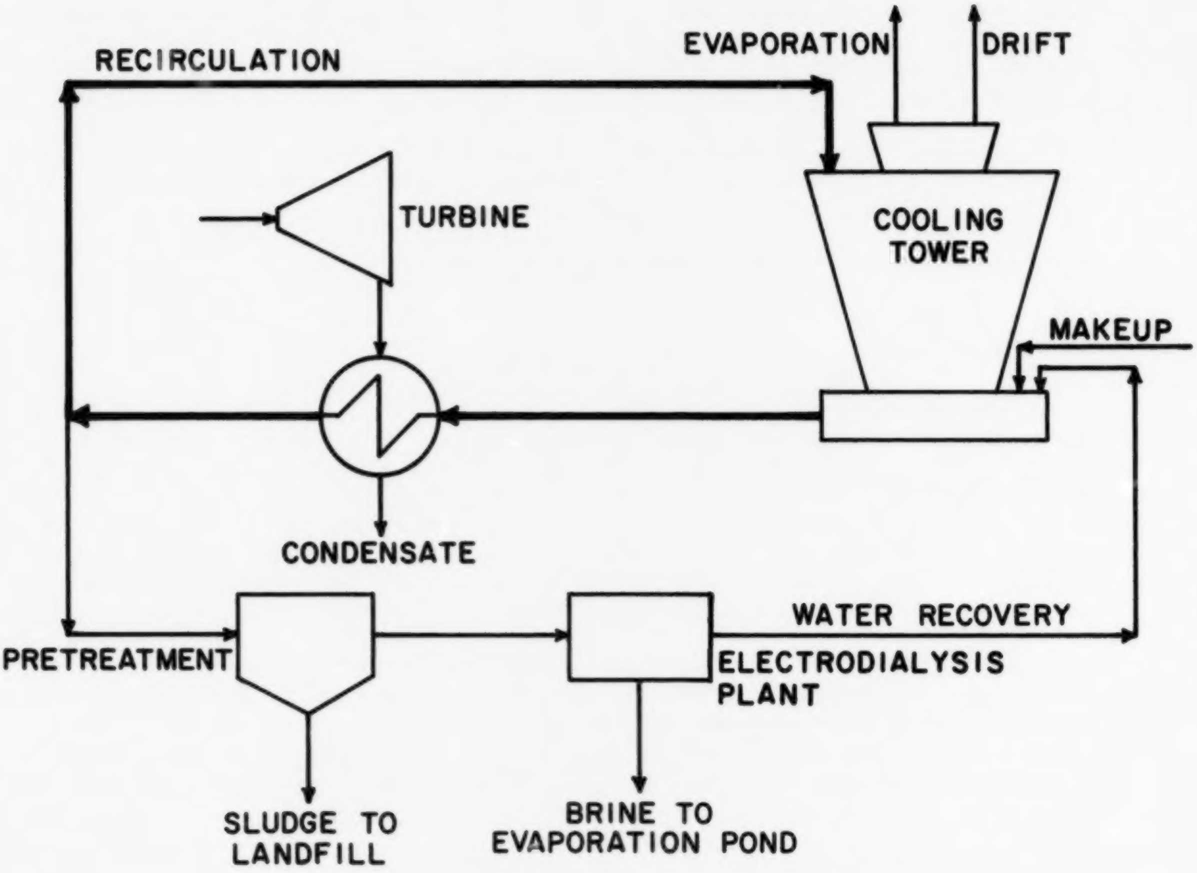
EVAPORATION
DRIFT
RECIRCULATION
TURBINE
COOLING TOWER
MAKEUP
CONDENSATE
WATER RECOVERY
PRETREATMENT
ELECTRODIALYSIS PLANT
SLUDGE TO LANDFILL
BRINE TO EVAPORATION POND

Figure 2. Flow diagram for cooling tower sidestream softening and desalting with electrodialysis. Adapted from Jordan, McIlhenny & Westbrook "Cooling Tower Effluent Reduction by Electrodialysis." Presented at the American Power Conference, Chicago, Illinois, April 22, 1976. Used by permission.

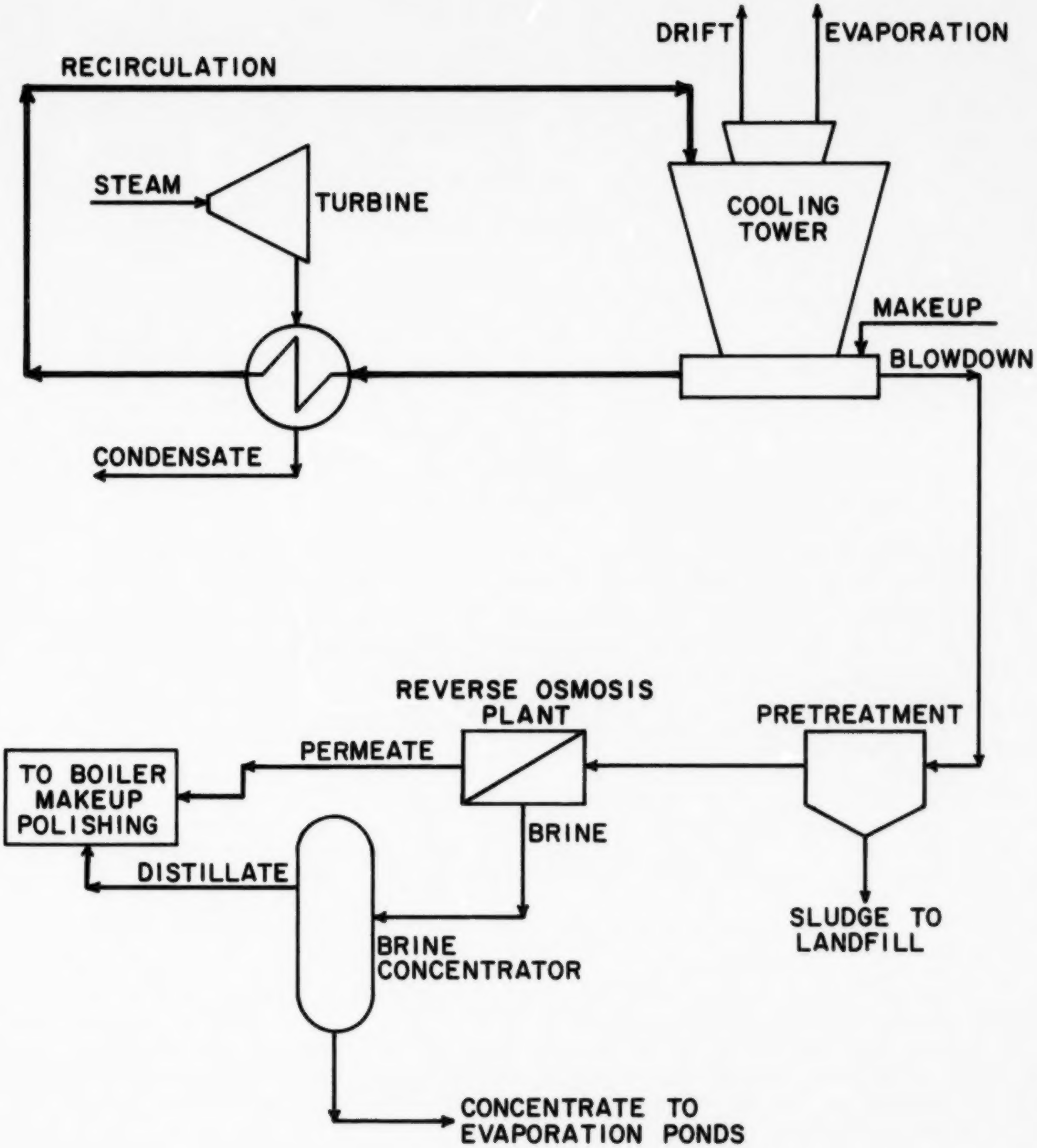
DRIFT
EVAPORATION
RECIRCULATION
STEAM
TURBINE
COOLING TOWER
MAKEUP
BLOWDOWN
CONDENSATE
REVERSE OSMOSIS PLANT
PRETREATMENT
PERMEATE
TO BOILER MAKEUP POLISHING
BRINE
DISTILLATE
BRINE CONCENTRATOR
SLUDGE TO LANDFILL
CONCENTRATE TO EVAPORATION PONDS

Figure 3. Flow diagram for cooling tower blowdown treatment by reverse osmosis for reuse.

SECTION 7

ASH SLUICE WATERS

CHARACTERISTICS OF WASTEWATER

Ash produced from a pulverized coal-fired power generation plant includes fly ash and bottom ash, with a weight ratio of about four to one. Fly ash generally is collected in hoppers below mechanical collectors and electrostatic precipitators, conveyed pneumatically to a water ejector, and sluiced to a settling pond. Bottom ash is collected in the bottom of the furnace and periodically removed from the furnace by water, through a clinker grinder, and piped to a settling pond.[41]

In some cases where space is at a premium, ash is dewatered in dewatering bins and shipped off site to be landfilled.

The quantity and characteristics of ash pond effluent are affected by the type of fuel used, the ash content of the fuel, the mode of firing, the design of the combustion chamber, the fraction of fly ash vs. bottom ash, the quantity and quality of sluice water used, and the performance of the settling pond.[29] The primary contents of fly ash and bottom ash are metal oxides of silica, calcium, magnesium, iron, and aluminum; oxidation products of sulfur and phosphorus; and carbon residuals.[42-45] The pyritic material, consisting primarily of iron sulfides that are removed from the coal before combustion, may also be disposed of into the ash pond. Metallic and sulfuric compounds present in the ash may be released and become constituents of the sluice water.[41]

TVA operates ash ponds that receive fly ash, bottom ash, or both. Specific data on the chemical characteristics of ash ponds are summarized in Table 6. The pH of these effluents varies from 3.3 to 12; half of the effluents are alkaline. The acidic or alkaline characteristics depend on the content of sulfur trioxide and alkaline metal oxides in the ash materials and on the buffering capacity of the water used for sluicing. Factors that affect the ash characteristics include source of the coal, methods of firing, ash fusion temperature, and efficiency of equipment for collecting fly ash.[41]

The operating conditions for TVA's 12 coal-fired power plants are summarized in Table 7. For the plants that use pulverized coal, the pH of ash pond effluents is mainly affected by the source of coal. Ash pond effluents from plants that receive coal from western Kentucky and southern Illinois are alkaline, whereas those from plants that receive coal from eastern Tennessee, eastern Kentucky, and Virginia are neutral or acidic.[41]

TABLE 6. CHARACTERISTICS OF ONCE-THROUGH ASH POND DISCHARGES

	Plant A		Plant B		Plant C
	Fly ash pond	Bottom ash pond	Fly ash pond	Bottom ash pond	Eastern Outlet
Flow, gpm[a]	6667.3	17798.7	NA	NA	7730
Total alkalinity,[a] mg/ℓ as $CaCO_3$	18.7	71.7	84.3	55.7	70.7
Phen. alkalinity,[a] mg/ℓ as $CaCO_3$	<1	<1	38	5	<1
Conductivity,[a] µmhos/cm	811	322	788	223.5	495
Total hardness,[a] mg/ℓ as $CaCO_3$	315	141.5	329	92.5	212.5
pH, units[a]	4.2	7.1	9.3	8.1	7.1
Dissolved solids,[a] mg/ℓ	517	168.7	524.3	136.3	342.3
Suspended solids, mg/ℓ	48.3	57	70.7	57	39.3
Aluminum, mg/ℓ	7.9	3.2	1.6	2.2	1.5
Ammonia, mg/ℓ as N	0.75	0.11	0.07	0.07	0.11
Arsenic, mg/ℓ	0.011	0.007	0.029	0.014	0.013
Barium, mg/ℓ	0.2	0.1	0.1	0.1	0.2
Beryllium , mg/ℓ	0.01	<0.01	<0.01	<0.01	<0.01
Cadmium, mg/ℓ	0.038	0.001	0.001	0.002	0.006
Calcium, mg/ℓ	126	38	152	50	78
Chloride, mg/ℓ	7	7	6	7	11
Chromium, mg/ℓ	0.072	0.007	0.013	0.009	0.006
Copper, mg/ℓ	0.33	0.07	0.03	0.06	0.05
Cyanide, mg/ℓ	<0.01	<0.01	<0.01	<0.01	0.01
Iron, mg/ℓ	2.3	5.2	1.4	4.7	1.7
Lead, mg/ℓ	0.066	0.017	0.015	0.018	0.021
Magnesium, mg/ℓ	14	6.0	3.6	6.2	10
Manganese, mg/ℓ	0.49	0.17	0.12	0.40	0.20
Mercury, mg/ℓ	0.0003	0.0005	0.0008	0.0009	0.0034
Nickel, mg/ℓ	0.08	0.06	0.05	0.06	0.05
Total phosphate, mg/ℓ as P	0.03	0.07	0.06	0.06	0.04
Selenium, mg/ℓ	0.002	0.002	0.015	0.007	0.010
Silica, mg/ℓ	13	7.4	7.1	6.4	7.4
Silver, mg/ℓ	<0.01	<0.01	<0.01	<0.01	0.01
Sulfate, mg/ℓ	346	45	214	102	158
Zinc, mg/ℓ	1.4	0.08	0.05	0.13	0.13

[a] Average values of weekly grab samples; all other numbers are average values of quarterly grab samples.

TABLE 6 (continued)

	Plant C Western Outlet	Plant D	Plant E	Plant F	Plant G
Flow, gpm[a]	1651.7	8224	5857.5	30616.5	7391
Total alkalinity,[a] mg/ℓ as $CaCO_3$	69	61.7	141	96.5	46.3
Phen. alkalinity,[a] mg/ℓ as $CaCO_3$	<1	5	105.5	82.5	20
Conductivity,[a] µmhos/cm	329.5	265	819	915	366
Total hardness,[a] mg/ℓ as $CaCO_3$	129	126.5	288	304	198
pH, units[a]	7.4	8.5	11.2	10.9	9.6
Dissolved solids,[a] mg/ℓ	217	157.3	389.5	408.5	263
Suspended solids, mg/ℓ	40	19	8	23	19.3
Aluminum, mg/ℓ	3.4	1.4	2.5	1.7	1.7
Ammonia, mg/ℓ as N	0.09	0.06	0.06	0.17	0.12
Arsenic, mg/ℓ	0.022	0.034	0.028	0.008	0.030
Barium, mg/ℓ	0.14	0.2	0.2	0.2	0.2
Beryllium , mg/ℓ	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium, mg/ℓ	0.002	0.001	0.001	0.001	<0.001
Calcium, mg/ℓ	37	31	126	107	73
Chloride, mg/ℓ	11	3	6	5	4
Chromium, mg/ℓ	0.009	<0.005	0.017	0.033	0.011
Copper, mg/ℓ	0.06	0.03	0.08	0.03	0.05
Cyanide, mg/ℓ	0.01	<0.01	<0.01	<0.01	0.01
Iron, mg/ℓ	6.0	0.32	0.16	0.22	0.53
Lead, mg/ℓ	0.017	0.016	0.017	0.013	0.014
Magnesium, mg/ℓ	10	8.3	0.3	1.57	2.4
Manganese, mg/ℓ	0.18	0.02	0.01	0.01	0.02
Mercury, mg/ℓ	0.0070	0.0002	0.0002	0.0003	0.0024
Nickel, mg/ℓ	0.06	0.06	<0.05	0.05	<0.05
Total phosphate, mg/ℓ as P	0.12	0.03	0.01	0.02	0.07
Selenium, mg/ℓ	0.003	0.070	0.007	0.014	0.010
Silica, mg/ℓ	6.7	4.0	7.0	6.0	4.4
Silver, mg/ℓ	0.01	0.01	0.01	<0.01	<0.01
Sulfate, mg/ℓ	99	57	147	160	182
Zinc, mg/ℓ	0.14	0.03	0.05	0.05	0.05

[a] Average values of weekly grab samples; all other numbers are average values of quarterly grab samples.

TABLE 6 (continued)

	Plant H	Plant I	Plant J	Plant K	Plant L
Flow, gpm[a]	2692.3	16872	14062.3	22447.3	14494
Total alkalinity,[a] mg/ℓ as $CaCO_3$	67.7	121.7	40	99.7	86
Phen. alkalinity,[a] mg/ℓ as $CaCO_3$	11.3	91	4.5	63.3	44
Conductivity,[a] μmhos/cm	392	652.5	311.5	472.5	359.5
Total hardness,[a] mg/ℓ as $CaCO_3$	115.5	211.5	103	174	178
pH, units[a]	8.6	10.7	6.2	10.8	10.2
Dissolved solids,[a] mg/ℓ	270	259	187.3	247.7	212.7
Suspended solids, mg/ℓ	14.3	19	39	19.3	15
Aluminum, mg/ℓ	1.6	1.5	2.6	1.8	2.0
Ammonia, mg/ℓ as N	0.34	0.07	0.05	0.06	0.52
Arsenic, mg/ℓ	0.123	0.36	0.041	0.033	0.032
Barium, mg/ℓ	0.2	0.2	0.2	0.2	0.1
Beryllium , mg/ℓ	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium, mg/ℓ	0.001	<0.001	0.001	0.001	0.001
Calcium, mg/ℓ	50	84	34	76	54
Chloride, mg/ℓ	14	6	5	10	6
Chromium, mg/ℓ	0.006	0.017	0.005	0.019	0.009
Copper, mg/ℓ	0.04	0.06	0.11	0.05	0.06
Cyanide, mg/ℓ	<0.01	<0.01	<0.01	<0.01	<0.01
Iron, mg/ℓ	0.56	0.26	2.4	0.39	0.56
Lead, mg/ℓ	0.015	0.012	0.015	0.017	0.017
Magnesium, mg/ℓ	7.4	1.2	6.7	1.6	2.6
Manganese, mg/ℓ	0.06	0.05	0.38	0.02	0.03
Mercury, mg/ℓ	0.0004	0.0003	0.0003	0.0003	0.0003
Nickel, mg/ℓ	0.05	0.05	0.05	0.06	<0.05
Total phosphate, mg/ℓ as P	0.12	0.06	0.06	0.05	0.06
Selenium, mg/ℓ	0.017	0.012	0.004	0.010	0.010
Silica, mg/ℓ	4.9	7.1	6.4	6.7	5.7
Silver, mg/ℓ	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate, mg/ℓ	98	81	119	83	80
Zinc, mg/ℓ	0.05	0.08	0.07	0.05	0.04

[a] Average values of weekly grab samples; all other numbers are average values of quarterly grab samples.

TABLE 7. RELATIONSHIPS BETWEEN PLANT OPERATION CONDITIONS AND pH VLUES OF ASH POND EFFLUENTS AT TVA COAL-FIRED POWER PLANTS[a]

Constituent	Plant D	Plant H	Plant J	Plant E
Coal source	E. Kentucky	Virginia E. Kentucky E. Tennessee	E. Kentucky E. Tennessee	W. Kentucky
Method of firing	Tangential	Tangential	Tangential	Circular Tangential
Ash content of coal, %	15.5	15	19.1	15.3
Fly ash of total ash, %	75	67	75	67
Bottom ash of total ash, %	25	33	25	33
Sluice water-to-ash ratio, gal/ton	10,770	11,425	9,520	9,585
pH value of raw water	7.5	7.0	7.6	7.0
pH value of ash pond effluent	8.6[b]	8.9[b]	6.3[b]	11.1[b]

[a] All values based on average values during 1974.
[b] Combined bottom and fly ash pond.
[c] Fly ash pond only.
[d] Bottom ash pond only.

Source: Chu, T.-Y. J., P. A. Krenkel, and R. J. Ruane. Characterization and Reuse of Ash Pond Effluents on Coal-Fired Power Plants. Paper presented at 49th Annual Water Pollution Control Federation Conference, Minneapolis, Minnesota, Oct. 2-8, 1976.

TABLE 7 (continued)

Constituent	Plant F	Plant G	Plant I	Plant K
Coal source	W. Kentucky S. Illinois	W. Kentucky	W. Kentucky	S. Illinois W. Kentucky
Method of firing	Opposed	Tangential	Tangential Horizontal	Circular
Ash content of coal, %	16.3	15.7	14	15.6
Fly ash of total ash, %	80	80	70	75
Bottom ash of total ash, %	20	20	30	25
Sluice water-to-ash ratio, gal/ton	19,490	12,345	42,430	17,265
pH value of raw water	7.4	7.3	7.4	7.6
pH value of ash pond effluent	11.2[b]	9.6[b]	11.2[b]	10.8[b]

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[a] All values based on average values during 1974.
[b] Combined bottom and fly ash pond.
[c] Fly ash pond only.
[d] Bottom ash pond only.

Source: Chu, T.-Y. J., P. A. Krenkel, and R. J. Ruane. Characterization and Reuse of Ash Pond Effluents on Coal-Fired Power Plants. Paper presented at 49th Annual Water Pollution Control Federation Conference, Minneapolis, Minnesota, Oct. 2-8, 1976.

TABLE 7 (continued)

Constituent	Plant L	Plant B	Plant C	Plant A
Coal source	W. Kentucky N. Alabama	W. Kentucky	W. Kentucky S. Illinois	W. Kentucky
Method of firing	Horizontal Tangential	Vertical	Cyclone	Cyclone
Ash content of coal, %	16	14.8	11	18.8
Fly ash of total ash, %	75	50	30	30
Bottom ash of total ash, %	25	50	70	70
Sluice water-to-ash ratio, gal/ton	15,730	-	23,065	9,810[d] 12,380[c]
pH value of raw water	7.5	7.5	7.4	7.7
pH value of ash pond effluent	10.1[b]	9.8[c] 8.0[d]	7.1[b]	4.4[c] 7.2[d]

[a] All values based on average values during 1974.
[b] Combined bottom and fly ash pond.
[c] Fly ash pond only.
[d] Bottom ash pond only.

Source: Chu, T.-Y. J., P. A. Krenkel, and R. J. Ruane. Characterization and Reuse of Ash Pond Effluents on Coal-Fired Power Plants. Paper presented at 49th Annual Water Pollution Control Federation Conference, Minneapolis, Minnesota, Oct. 2-8, 1976.

The high concentrations of suspended solids in ash ponds that receive fly ash probably are caused by low-density, hollow-sphere ashes (cenospheres) that are not removed by natural settling. The amount of cenospheres generated at coal-fired plants can be as much as 4 to 5 percent by weight, or 15 to 20 percent by volume, of the fly ash. The principal constituents in cenospheres are similar to those in fly ash.[42] Because trace elements also are present in the cenospheres, they can contribute to the total concentration of trace elements in the ash pond discharges.[42]

In a recent study for EPA,[47] Radian Corporation reviewed different options for recycling ash sluice waters. Because bottom ash is not very reactive, recycle of bottom ash sluice water typically poses no serious problems. Fly ash is much more reactive, and because ashes from different coals have different characteristics, it is difficult to predict the characteristics of recirculated fly ash sluice water. Depending on the particular situation, recirculating fly ash sluice waters may require either no treatment or one of several treatment methods. The simplest treatment allows time for ash to react with water and for supersaturated species to precipitate (under control) in a large reaction tank before entering the sluice lines. Alternatively, softening of the recirculating water will reduce the potential for calcium and magnesium scaling. Whichever option is chosen, pilot testing would be required to determine design criteria for a full-scale recirculating system and to determine the recirculating water characteristics.

Blowdown can be used to reduce the total dissolved solids concentration, or brine concentration by reverse osmosis, evaporation, or electrodialysis may be used. Again, the need for dissolved solids control can be established by pilot testing.

ALTERNATIVE TREATMENTS

Reverse osmosis, electrodialysis, and vapor-compression distillation can be used to control dissolved solids by concentrating a blowdown or sidestream from recirculating ash sluice systems. Dissolved solids can also be controlled by increasing the makeup flow and discharging blowdown.

Conventional methods of rendering blowdown acceptable should be considered. These include control of pH and redox potential to precipitate metals and the use of higher blowdown rates to reduce their concentration. Suspended solids can generally be controlled by settling or filtration.

Electrodialysis

Dissolved salt can be removed from a sidestream of an ash sluice system by electrodialysis. This system would be essentially similar to that proposed in Section 2 for cooling water. Cost comparisons made in Section 2 would appear valid for ash sluice waters also, but much needs to be learned about the characteristics of ash sluice waters when recirculation is practiced.

Reverse Osmosis

Reverse osmosis can be used to concentrate blowdown from ash sluice systems. The system would be much like that described in Section 2 for concentration of cooling tower blowdown, and the cost advantages would be similar. Careful pH control may be necessary to prevent membrane fouling by metal oxides.

Laboratory tests on treating once-through ash pond effluent were conducted by TVA. Fly ash pond effluent from TVA Plant A was tested because of its acid characteristics and its relatively high concentrations of several trace metals. The major constituents in the ash pond effluent are suspended solids, sulfate, calcium, magnesium, and silica; therefore, spiral-wound and tubular modules were selected to treat this wastewater. The fly ash pond effluent was run through a 1- to 3-μm fiber filter to remove suspended solids; it was then run through each module of the Roga spiral-wound cellulose triacetate membrane, the DuPont spiral-wound polyamide membrane, and the UOP Fluid Science tubular cellulose acetate membrane individually. The data of rejection on total dissolved solids from each module are shown in Table 8. The Roga spiral-wound module appears better for treating this type of wastewater, and additional experiments were conducted with this module to treat fly ash pond effluent which had been concentrated by a factor of 1.7. The experimental results are shown in Table 9.

Although treatment of once-through ash pond water is not expected to be economical, these results show satisfactory flux and rejection performance and indicate no special problems should be expected from this type of waste treatment.

RECOMMENDATIONS

Treatment of recirculating ash sluice water by reverse osmosis or electrodialysis is feasible. At each plant, the need for dissolved solids control should be critically examined. If control is needed, alternative methods should be explored, including reverse osmosis and electrodialysis.

Large-scale demonstrations of reverse osmosis or electrodialysis for concentrating ash sluice blowdown should be deferred until a better understanding of recirculating ash sluice systems is attained and the need for dissolved solids control in these streams is established.

Experience gathered in demonstrating electrodialysis and reverse osmosis to control dissolved solids in cooling waters should be transferable to ash sluice pond water treatment.

Dry ash handling systems should be given consideration for reducing water requirements and discharges.

TABLE 8. RESULTS OF REVERSE OSMOSIS STUDIES ON FLY ASH POND EFFLUENT FROM TVA PLANT A

Membrane	Feed composition	Permeate (gal/min)	Rejection (%)	Operation pressure (psig)	Feed flow (gal/min)
Roga Spiral Wound	Conductivity, 852.5 µmho/cm pH, 4.3	1.2	93	400	4.0
DuPont Spiral Wound	Conductivity, 840 µmho/cm pH, 4.5	0.45	92.6	400	4.0
UOP Fluid Science Tubular	Conductivity, 827.5 µmho/cm pH, 4.3	0.16	79.3	400	4.0

TABLE 9. RESULTS OF REVERSE OSMOSIS STUDIES ON CONCENTRATED FLY ASH POND EFFLUENT FROM TVA PLANT A

Membrane	Feed composition	Permeate (gal/min)	Rejection (%)	Operation pressure (psig)	Feed flow (gal/min)
Roga Spiral Wound	Conductivity, 1450 µmho/cm	1.15	-	400	4.0
	TDS, 1500 mg/ℓ	1.15	96.7	400	4.0
	Al, 9.6 mg/ℓ	1.15	95.8	400	4.0
	Ca, 280 mg/ℓ	1.15	96.8	400	4.0
	Cd, 0.29 mg/ℓ	1.15	97.9	400	4.0
	Cr, 0.25 mg/ℓ	1.15	93.2	400	4.0
	Cu, 6.9 mg/ℓ	1.15	96.2	400	4.0
	Fe, 0.56 mg/ℓ	1.15	>91	400	4.0
	Pb, 0.042 mg/ℓ	1.15	>90	400	4.0
	Mg, 51 mg/ℓ	1.15	96.5	400	4.0
	Mn, 1.5 mg/ℓ	1.15	96	400	4.0
	Se, 0.003 mg/ℓ	1.15	>90	400	4.0
	Si, 27.8 mg/ℓ	1.15	88.5	400	4.0
	SO_4, 815 mg/ℓ	1.15	96.9	400	4.0
	Zn, 6.65 mg/ℓ	1.15	99.1	400	4.0
	pH, 4.7 mg/ℓ	1.15	-	400	4.0

SECTION 8

COAL PILE DRAINAGE

CHARACTERISTICS OF WASTEWATER

To ensure uninterrupted generation of electricity, an outdoor coal reserve is maintained at each power plant. A 90-day coal supply is customarily maintained. Coal piles are typically 8 to 12 m (25 to 40 ft) high and cover an area of 10 to 40 ha (25 to 100 acres). Normally, 600 to 1800 m^3 (780 to 2340 yd^3) of coal storage is required for every megawatt of rated capacity.[47]

Coal pile drainage results from percolation of rainfall through stored coal. The water quality of the drainage is affected by the leaching of oxidation products of metallic sulfides associated with the coal. The sulfide-bearing minerals that predominate in coal are pyrite and marcasite, both iron sulfide ores. Marcasite is unstable and degrades into pyrite. The oxidation of pyrite results in production of ferrous iron and acidity. This ferrous iron then undergoes oxidation to the ferric state. Ferric iron then hydrolyzes to form insoluble ferric hydroxide, thus producing more acidity.[48]

The following characteristics of the coal pile runoff were reported for a power plant at Springfield, Illinois: suspended solids--2200 to 21,000 mg/ℓ, with an average of 10,300 mg/ℓ; total iron--50 to 80 mg/ℓ, with an average of 61 mg/ℓ; and total aluminum--240 mg/ℓ.[49]

TVA conducted an intensive study on coal pile drainage.[50] The study programs were established at two coal-fired steam plants. Plant J has a rated capacity of 1700 MW, with a 90-day coal supply amounting to about 9.6×10^5 m^3 (1.26×10^6 yd^3), or 1.1×10^9 kg (1.2×10^6 tons). Plant E has a rated capacity of 1400 MW, with a 90-day coal supply amounting to about 8.6×10^5 m^3 (1.13×10^6 yd^3), or 9.88×10^8 kg (1.08×10^6 tons). Coal for plant J is mined in eastern Tennessee and Kentucky, and coal for plant E is mined in western Kentucky. A typical analysis of coal from both plants is shown in Table 10.

Both of the TVA coal pile drainage systems investigated exhibited highly acidic drainages. Acidity was quite variable in both cases (Table 11), but pH was limited to a rather tight band (2.3 to 3.1). Means (arithmetic) are similar; 21 of the 33 values fall between 2.6 and 3.0. Values of pH of coal pile drainage reported by EPA[26] exhibit a slightly broader range of 2.1 to 3.0. Anderson and Youngstrom[51] report a pH of 2.2 to 5.8 for hourly pH measurements over a 3-week period. Matsugu[52] reports a pH of 2.4 to 3.0 for 67 grab samples of coal pile

TABLE 10. COAL ANALYSIS, DRY BASIS

Constituent	Plant J	Plant E
Total moisture, %	3.8	4.2
Volatile matter, %	34.1	37.7
Ash %	17.2	15.0
Fixed carbon, %	48.7	47.3
Total sulfur, %	2.1	3.9
Energy, Btu/lb	12,270	12,450
Ash analysis		
CaO, % of ash	1.4	4.2
MgO, % of ash	1.1	1.1

TABLE 11. GENERAL CHEMICAL CHARACTERISTICS OF COAL PILE DRAINAGES COLLECTED FROM TWO TVA STEAM PLANTS

	pH	Acidity (mg/ℓ as $CaCO_3$)	Sulfate (mg/ℓ)	Dissolved solids (mg/ℓ)	Suspended solids (mg/ℓ)	Iron (mg/ℓ)	Manganese (mg/ℓ)
				PLANT J			
Range	2.3-3.1	300-7100	1800-9600	2500-16,000	8.0-2300	240-1800	8.9-45
Mean	2.8	3447	5160	7790	430	943	28
Number of samples	21	20	18	20	20	21	21
				PLANT E			
Range	2.3-3.1	700-4800	1800-6200	270-8200	38-680	23-590	1.8-12
Mean	26	1648	3050	3905	282	350	4.5
Number of samples	12	12	12	12	12	12	12
				PLANT E (DISCRETE STORM)			
Range	2.5-2.7	300-1400	870-5500	1200-7500	69-2500	62-380	0.88-5.4
Mean	2.63	710	2300	2700	650	150	2.3
Number of samples	14	14	14	14	14	14	14

Source: Cox, D. B., T.-Y. J. Chu, and R. J. Ruane. Quality and Treatment of Coal Pile Runoff. In: Proc., Seventh Symposium on Coal Mine Drainage Research, NCA/BCR Coal Conf. and Expo IV, Louisville, Kentucky, October 13-20, 1977. pp. 232-255.

leachate. For these same samples, acidity varied from 10 to 120 milliequivalents/liter (meq/ℓ). Thus, the pH of coal pile drainage, at least for eastern coal, is generally in the relatively narrow range of 2.1 to 3.1.

Concentrations of suspended solids at plant J ranged from 8 to 2300 mg/ℓ, with a mean of 430 mg/ℓ. At plant E, where direct runoff was collected as a single composite sample for each storm event, the mean and range of suspended solids concentrations were somewhat lower. Much higher values for suspended solids were reported by Matsugu.[52]

Iron concentrations at plant E ranged from 23 to 590 mg/ℓ, with a mean of 354 mg/ℓ. Concentrations of iron at plant J were higher, with a range of 240 to 1800 mg/ℓ and a mean of 943 mg/ℓ. Values for iron reported by EPA[26] ranged from 0.17 to 93,000 mg/ℓ, with a mean of 19,500 mg/ℓ. A somewhat narrower range of 10 to 5300 mg/ℓ and a lower mean of 1150 were reported by Anderson and Youngstrom.[51]

Manganese concentrations reported by Anderson and Youngstrom[51] ranged from 4.5 to 72.0 mg/ℓ, with a mean of 17.1 mg/ℓ. Somewhat lower concentrations, ranging from 3.4 to 12 mg/ℓ, with a mean of 6.9 mg/ℓ, were reported by Matsugu.[52] Levels at plant J (Table 12) were comparable to those presented by Anderson and Youngstrom.[51] Values for plant E were somewhat lower.

Trace elements of environmental concern in coal that have been identified by EPA[53] are presented in Table 12. Results of analyses for selected trace elements are presented in Table 13. Of these elements, lead, barium, and titanium were low or consistently below the limits of detection. Most means of trace element concentrations at plant J are three to eight times as high as those at plant E.[47]

Concentrations of copper at plant J are higher than the criteria set by EPA[54], but are lower than those reported by EPA[26] or Anderson and Youngstrom.[51] Concentrations for plant E are lower still.

The mean zinc concentrations of 6.46 mg/ℓ at plant J and 2.42 mg/ℓ at plant E are similar to the means of 5.9 mg/ℓ reported by EPA[26] and 3.67 mg/ℓ reported by Anderson and Youngstrom.[51] The criterion established by EPA[54] for a public water supply is 5 mg/ℓ.

Cadmium concentrations at both plants were below water quality criteria.[54]

Mean concentrations of 260 mg/ℓ at plant J and 43 mg/ℓ at plant E were found for aluminum.

Concentrations of nickel are also above levels found in surface water.[55]

Chromium concentrations are well below established water quality criteria[54] at both plants.

TABLE 12. RANGE OF TRACE ELEMENTS IN U.S. COALS

Major Elements		Minor Elements	
Element	Concentration Range (Weight %)	Element	Concentration Range (ppm)
Al	0.43 - 3.04	As	0.5 - 106
Ca	0.05 - 2.67	B	1.2 - 356
Cl	0 - 0.56	Be	0 - 31
Fe	0.32 - 4.32	Br	4 - 52
K	0.02 - 0.43	Cd	0.1 - 65
Mg	0.1 - 0.25	Co	0 - 43
Na	0 - 0.20	Cr	0 - 610
Si	0.58 - 6.09	Cu	1.8 - 185
Ti	0.002- 0.32	Ga	0 - 61
		Ge	0 - 819
		Hg	0.01- 1.6
		La	0 - 98
		Mn	6 - 181
		Mo	0 - 73
		Ni	0.4 - 104
		Pb	4 - 218
		Sb	0.2 - 9
		Sc	10 - 100
		Se	0.4 - 8
		Sn	0 - 51
		U	<10 -1000
		V	0 -1281
		Y	<0.1 - 59
		Zn	0 -5600
		Zr	8 - 133

Source: Wewerka, E. M. et al. Environmental Contamination From Trace Elements in Coal Preparation Wastes - A Literature Review and Assessment. EPA-600/7-76-007, August 1976. 61 pp.

TABLE 13. TRACE METAL CONCENTRATIONS IN COAL PILE DRAINAGE
(values in mg/ℓ)

	Cu	Zn	Cd	Al	Ni	Cr	Hg	As	Se	Be
PLANT J										
Minimum	0.42	2.3		66	0.7	<0.005	<0.0002	0.005	0.001	0.03
Maximum	1.4	16	<0.001	440	4.5	0.011	0.0025	0.36	0.03	0.07
Mean	0.86	6.46	<0.001	260	2.5	0.006	0.0004	0.15	0.005	0.04
N_D[a]	0	0	21	0	0	12	13	0	0	0
Number of samples	21	21	21	21	21	18	21	20	20	19
PLANT E										
Minimum	0.07	1.1	<0.001	20	0.15	<0.005	0.0005	0.006	<0.001	<0.01
Maximum	0.46	5.1	0.003	92	0.49	0.011	0.0072	0.046	0.006	0.03
Mean	0.18	2.42	0.002	43	0.34	0.01	0.003	0.02	0.002	0.01
N_D[a]	0	0	6	0	0	8	0	0	3	8
Number of samples	12	12	12	11	12	12	11	9	10	11

[a] N_D indicates number of samples below detection limits.

Source: Cox, D. B., T.-Y. Chu, and R. J. Ruane. Quality and Treatment of Coal Pile Runoff In: Proc., Seventh Symposium on Coal Mine Drainage Research, NCA/BCR Coal Conf. and Expo IV, Louisville, Kentucky, Oct. 13-20, 1977. pp. 232-255.

Levels of beryllium are well below the established criterion for waters of a hardness of 245 to 300 mg/ℓ.[55]

Mercury concentrations were an order of magnitude higher at plant E than at plant J. Levels at both plants exceeded the established water quality criterion.[54]

Arsenic levels in drainage from plant J ranged from 0.005 to 0.36 mg/ℓ, with a mean of 0.15 mg/ℓ. These values generally exceeded established criteria, whereas those concentrations found at plant E generally did not. Concentrations of selenium behaved similarly. This is significant since selenium and arsenic exhibit antagonistic toxicities.[56]

The Clean Water Act of 1977 requires EPA to establish effluent limitaions for 65 toxic (priority) pollutants. Elements on this list which have been found in significant concentrations in coal pile drainage include arsenic, selenium, nickel, copper, zinc, and mercury.

ALTERNATIVE TREATMENTS

Most metals can be precipitated by the conventional process of pH adjustment and removed as suspended solids. Theoretically, the solubilities of arsenic and selenium are not affected by pH adjustment,[57] but a number of other processes have been proposed for their removal.[58-62]

TVA has tested the ability of several reverse osmosis membranes to remove trace metals, and the results are presented in the appendix. Rejections were generally better than 80 percent. Adjustment of pH followed by suspended solids removal is required as pretreatment for reverse osmosis. In pretreating one waste by pH adjustment, TVA found that this process alone would produce acceptable effluent. Even the arsenic concentration was significantly reduced. The waste was boiler fireside wash water from an oil-fired generating unit. This waste is similar to coal pile drainage in its pH (2.4) and in its high concentration of metals, notably iron. Characteristics of this waste are presented in Table 14 and results of pretreatment studies in Table 15.

There is no information in the literature on treatment of coal pile drainage with membrane processes. However, reverse osmosis treatment of mine drainage, which has characteristics similar to those of coal pile drainage, has been studied for many years. The EPA has been sponsoring and conducting research since 1966 on the use of reverse osmosis for treatment of mine drainage. Potentials for recovery of valuable heavy metals are also being investigated.[63] Blackshaw and Pappano[64] reported on a study concerning the technical and economic feasibility of using reverse osmosis for treatment and purification of acid mine drainage. The reverse osmosis unit was rated at 60,000 gpd product water output, featuring feedflow and waste brine flow controllers that can be preset to desired flow rates, depending on recovery requirements and reverse osmosis modular-tube arrays. Wilmoth and Scott[65] investigated an application of reverse osmosis to a ferrous-iron acid mine drainage in Mocanaqua, Pennsylvania. The operating parameters and chemical data are shown in

TABLE 14. BOILER WASH WASTE

Parameter	Concentration (mg/ℓ) Unless Otherwise Indicated
Total Dissolved Solids	6100
Total Suspended Solids	1300
SO_4	6000
Cl	71
SiO_2	100
Dissolved Fe	1300
Suspended Fe	230
Ca	30
Mg	34
Na	5.5
K	0.1
Al	7.4
As	0.09
B	0.32
Ag	0.01
Be	<0.01
Ba	7.9
Cd	<0.001
Cu	8.6
Hg	<0.0002
Mn	15
Ni	55
Pb	0.01
Se	0.008
Ti	<1.0
V	20
Zn	4.3
Kjeldahl Nitrogen - N	0.45
Nitrite Plus Nitrate Nitrogen - N	0.16
Local Phosphate - P	0.61
pH	2.4 (Units)
Conductivity	4550 (μmho/cm)
Turbidity	47 (JTU)

TABLE 15. RESULTS OF CHEMICAL TREATMENT ON BOILER WASH WATER

Parameters	Concentration				
	Initial	Final			
pH, unit	2.4	7	8	9	10
As, mg/ℓ	0.09	<0.005	<0.005	<0.005	<0.005
Ba, mg/ℓ	7.9	0.7	1.3	1.0	1.1
Ca, mg/ℓ	30	730	800	950	980
Cu, mg/ℓ	8.6	0.35	0.05	0.03	0.04
Fe, mg/ℓ	1530	2.9	0.2	0.05	0.14
Mg, mg/ℓ	34	-	20	24	21
Mn, mg/ℓ	15	2	0.56	0.15	0.02
Ni, mg/ℓ	55	0.53	0.22	0.10	0.06
V, mg/ℓ	20	<0.1	0.2	0.3	0.4

All concentrations of metals are total metals.

Tables 16 and 17, respectively. A contract study for EPA[66] tested spiral-wound reverse osmosis systems on acid mine drainage discharges at four locations: Norton, West Virginia; Morgantown, West Virginia; Ebensbury, Pennsylvania; and Mocanaqua, Pennsylvania. The water quality characteristics of those sites were quite different. At all sites, the limiting factor in high recovery operation was calcium sulfate insolubility. Neutralization of the product water was needed in all cases to elevate pH, and in some cases, to remove residual iron and manganese. Neutrolosis, which is the blending of neutralized brine supernatant from the reverse osmosis unit back into the feed to the unit, has been shown to be a promising process for obtaining maximum recoveries and reducing the brine disposal problem. The pretreatment at all sites consisted of 10-μm filtration. Ultraviolet disinfection, acid injection, or both were needed at some sites to prevent iron oxidation and precipitation.

Kaup[67] proposed a combined treatment process with reverse osmosis and ion exchange for acid mine drainage. After pretreatment for fouling control, 75 percent of the wastewater will be recovered by reverse osmosis, and the remaining 25 percent concentrate will be treated by ion exchange.

Cost information for treating coal pile drainage with reverse osmosis is unavailable from the literature.

Wilmoth[66] reported that estimates of reverse osmosis treatment costs for acid mine drainage ranged from $0.75 to $2.00 per thousand gallons in June 1976, excluding treatment and disposal of the highly polluting waste-brine stream.

RECOMMENDATIONS

More study needs to be made of conventional means of removing heavy metals from coal pile drainage. 'Particularly, methods using lime/limestone on soda ash for pH adjustment should be investigated.

Reverse osmosis can be used to remove residual heavy metals after the bulk has been removed by pH adjustment and suspended solids removal. A suggested flow diagram is shown in Figure 4. To help prevent calcium sulfate scale, either caustic soda or soda ash is chosen as the base for pH adjustment. This will allow greater water recovery and lower brine disposal costs. Brine is recycled so that those species on the threshold of precipitation (primarily metal oxides) can be removed under control in the sedimentation basin. Further water recovery is thus possible.

Design and optimization of such a system would require a considerable development effort, including pilot plant work and analysis. Optimization of the precipitation and sedimentation processes would be desirable. In fact, reverse osmosis pretreatment may remove heavy metals to the extent that the reverse osmosis itself is not required.

TABLE 16. OPERATING PARAMETERS FOR SPIRAL-WOUND REVERSE OSMOSIS STUDY AT 75% RECOVERY AT MOCANAQUA, PENNSYLVANIA

Constituent	Value[a]
Raw water feed flow, gal/min	6.02
Product waterflow, gal/min	4.50
Brine water discharged, gal/min	1.52
Brine water recycled, gal/min	4.26
Minimum brine/product flow ratio (Tubes 1 and 2), ratio/module	5:1
Maximum brine/product flow ratio (Tube 3), ratio/module	12:1
Water recovery, %	74.8
Recovery of blended feed, %	43.8
Feed pressure, psig	602
Feed water temperature, °F	62.6
Tube 1 flux, gal/ft^2·day at 600 psi net and 77°F	19.56
Tube 2 flux, gal/ft^2·day at 600 psi net and 77°F	19.52
Tube 3 flux, gal/ft^2·day at 600 psi net and 77°F	18.77
Length of run, h	1672

[a] All values are means from 73 data sets.

Source: Wilmoth, R. C., and R. B. Scott, Water Recovery from Coal Pile Drainage. Proc. 3rd National Conference on Complete Water Reuse, Cincinnati, Ohio, June 1976. Reprinted by permission of the author.

TABLE 17. CHEMISTRY ANALYSES FOR REVERSE OSMOSIS TREATMENT OF ACID MINE DRAINAGE

	Raw feed	Waste brine	Effluent
Conductivity (μmho/cm)	1000	3600	17
Acidity (mg/ℓ, as $CaCO_3$)	240	810	32
pH (unit)	3.4	2.9	4.5
Ca (mg/ℓ)	130	490	0.5
Mg (mg/ℓ)	90	310	0.6
Total iron (mg/ℓ)	77	330	0.5
Total Fe^{2+} (mg/ℓ)	64	250	0.5
Na (mg/ℓ)	-	-	-
Al (mg/ℓ)	12	44	0.2
Mn (mg/ℓ)	12	24	0.08
SO_4 (mg/ℓ)	750	2800	2.2
Alkalinity (mg/ℓ, as $CaCO_3$)	0	0	0
TDS (mg/ℓ)	1300	4500	5

Source: Wilmoth, R. C., and R. B. Scott. Water Recovery from Coal Pile Drainage. Proc., 3rd National Conf. on Complete Water Reuse, Cincinnati, Ohio, June 1976. Reprinted by permission of the author.

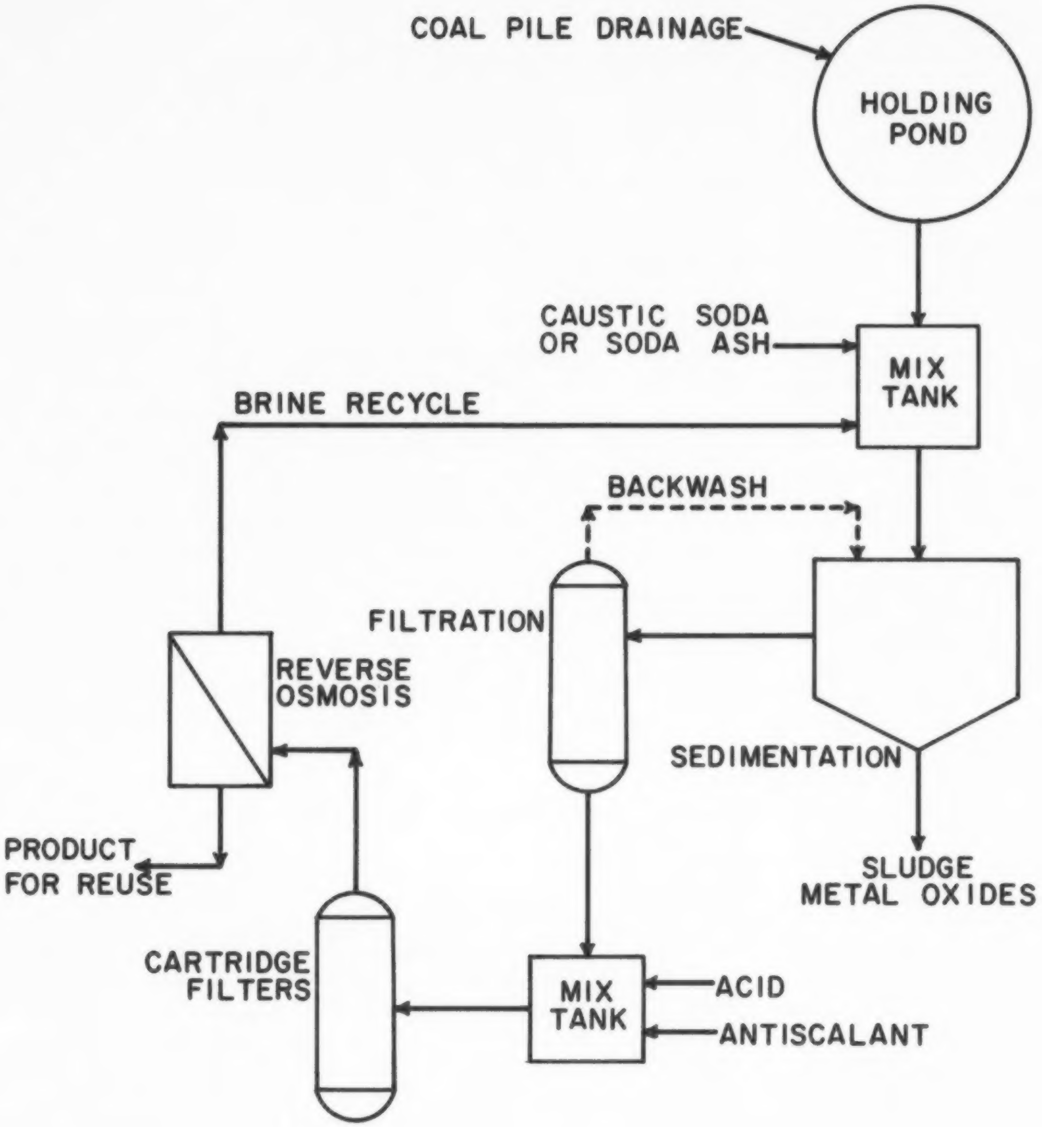
COAL PILE DRAINAGE
HOLDING POND
CAUSTIC SODA OR SODA ASH
MIX TANK
BRINE RECYCLE
BACKWASH
FILTRATION
REVERSE OSMOSIS
SEDIMENTATION
PRODUCT FOR REUSE
SLUDGE METAL OXIDES
CARTRIDGE FILTERS
MIX TANK
ACID
ANTISCALANT

Figure 4. Flow diagram for reverse osmosis treatment of coal pile drainage.

SECTION 9

BOILER MAKEUP WATER TREATMENT WASTES

CHARACTERISTICS OF WASTEWATER

The regenerants from boiler makeup water demineralizers typically contain about 10-20 percent solids, mostly sodium sulfate, and include all of the ions present in the water supply, but concentrated manyfold. The volume of regenerant waste produced depends on the size of the units in the system and the manner in which the rinse water is handled. Some multiple-bed ion-exchange demineralizers reduce the amount of rinse waste by using rinse-recycling techniques.[68] The frequency of regeneration, which will determine the amount of regeneration chemicals used and the wastes produced, depends on the quality of feedwater and other factors and varies from daily to weekly. If a reverse osmosis process is used ahead of the ion exchange system, savings in overall annual costs can be achieved. The quality of the raw feedwater varies from one plant to another, and thus the extent of pretreatment required also varies. Because a large amount of acid (typically sulfuric) and caustic (typically sodium hydroxide) are used in ion exchange regeneration, compared with the small quantity of chemicals used for pH control and scale prevention in reverse osmosis systems, the use of reverse osmosis will cut down the total dissolved solids in the wastewater.

ALTERNATIVE TREATMENTS

Both reverse osmosis and electrodialysis[69] have been suggested as roughing demineralizers for boiler makeup water. Both generally require pretreatment to prevent membrane scaling and fouling and are followed by polishing demineralizers. Reverse osmosis is generally preferred because it produces high quality water, free of colloids, in one stage. Electrodialysis reduces salt content by about 30 to 50 percent per stage but does not remove colloids. Colloids often cause fouling of the polishing demineralizers.

Rowland et al.[70] first reported the use of reverse osmosis as a precursor to a demineralizer system for the Burbank (California) Public Service Department. The process resulted in a cost savings of more than one-third compared with the conventional system of ion exchange only. There were five reasons for these savings: (1) when preceded by reverse osmosis, the demineralizers produce five to ten times more deionized water between regenerations; (2) manpower requirements for operation and maintenance are reduced to less than 50 percent of that for an ion exchange system only; (3) reliability of product water quality is improved; (4) chemical requirements are lowered by 90 to 95 percent, reducing costs and minimizing waste disposal problems; and (5) the life of the ion exchange resin is extended. The typical brine and product analyses for well-water feedstock are shown in Table 18.

TABLE 18. WELL WATER, BRINE, AND PRODUCT ANALYSES--
BURBANK PUBLIC SERVICE DEPARTMENT

Well-water constituent	Concentration of consitituent (mg/ℓ) in		
	Well water[a]	Brine[b]	Product[c]
Silica	24	70	5
Calcium	56	186	2
Magnesium	13	43	Trace
Sodium	33	110	5
Carbonate	0	0	0
Bicarbonate	90	231	19
Chloride	23	69	4
Sulfate	163	582	8
Phosphate	Trace	0	Trace
Nitrate	4	9	2
Total salines (approximate)	365	1185	35
Total hardness (as $CaCO_3$)	193	641	5

[a] pH = 5.8
[b] pH = 6.1
[c] pH = 5.1

Source: Rowland, H., I. Nasbaum, and F. J. Jester. Consider Reverse Osmosis for Producing Feedwater. Power, December 1971. Reprinted with permission from Power Magazine, Copyright McGraw-Hill, Inc., 1971.

Wadlington[13] reported that a reverse osmosis unit installed ahead of an existing ion exchange system reduced the chemical regenerant requirements, increased the resin life, reduced total chemical waste, and provided a capability for treating increases in total dissolved solids with little or no increase in operating cost, which is unlike ion exchange treatment alone. The savings in chemical regenerants alone were enough to pay back the reverse osmosis capital cost in 1.5 years.

Skrinde *et al.*[71] compared the costs of using these three processes to treat a specific source of water, which is characterized in Table 19, to meet the required quality water shown in Table 20. Process II (softening followed by ion exchange) and process III (reverse osmosis followed by ion exchange) have the common characteristics of providing a pretreatment step ahead of a final polish by demineralization. Process II consists of first-stage softening by the addition of lime and soda ash, thus precipitating hardness. This results in hardness reduction by replacing calcium and magnesium ions with sodium ions, while the total dissolved solids remain relatively unchanged. Softening is followed by ion exchange to remove the

TABLE 19. CHARACTERISTICS OF RAW WATERS

Analysis	Well Water	City water
Total dissolved solids, mg/ℓ	360.0	401.0
Total hardness, as $CaCO_3$, mg/ℓ	240.0	262.0
Alkalinity, as $CaCO_3$, mg/ℓ	161.0	136.0
Noncarbonate hardness, as $CaCO_3$, mg/ℓ	79.0	126.0
Silica, as SiO_2, mg/ℓ	11.0	19.4
Sulfate, as SO_4, mg/ℓ	49.5	64.2
Chloride, as Cl, mg/ℓ	24.0	21.4
Fluoride, as F, mg/ℓ	0.7	0.6
Calcium, as Ca, mg/ℓ	59.0	55.2
Magnesium, as Mg, mg/ℓ	22.0	25.5
Sodium, as Na, mg/ℓ	17.8	12.3
Iron, as Fe, mg/ℓ	0.1	0.1
Odor	None	None
Potassium, as K, mg/ℓ	1.75	2.2
Color, units	0.5	0.7
Carbon dioxide, as CO_2, mg/ℓ	0.0	0.0
Bicarbonate, as $CaCO_3$, mg/ℓ	149.0	127.0
Carbonate, as $CaCO_3$, mg/ℓ	12.0	10.1
Hydroxide, as $CaCO_3$, mg/ℓ	0.0	0.0
pH, units	7.9	7.5
pHs	7.5	7.7
Ryznar index (2 pHs-pH)	7.1	7.9
Langlier index (pH-pHs)	+0.4	-0.2
Hydrogen sulfide, as H_2S, mg/ℓ	=	0.4
Turbidity, JTU	1.8	1.7
Organic carbon, mg/ℓ	0.64	-

Source: Skrinde, R. T., W. M. Steeves, L. S. Shields, and T. L. Tang. Economic and Technical Evaluation of Reverse Osmosis for Industrial Water Demineralization. Paper presented at Industrial Water and Pollution Conf. and Exposition, Chicago, Illinois, March 14-16, 1973.

TABLE 20. WATER QUALITY REQUIREMENTS FOR COMBUSTION TURBINE INJECTION

Analysis	Concentration (mg/ℓ)
Dissolved solids	90
Suspended solids	9
Alkalinity	3
Silica	9
Sulfide	1
Phosphate	1.5
Chloride	6
Iron	0.01
Copper	0.005
Calcium	10
Sodium and potassium (combined)	2

Source: Skrinde, R. T., W. M. Steeves, L. S. Shields, and T. L. Tang. Economic and Technical Evaluation of Reverse Osmosis for Industrial Water Demineralization. Paper presented at Industrial Water and Pollution Conf. and Exposition, Chicago, Illinois. March 14-16, 1973.

remaining hardness and sodium, producing a final product virtually free of contaminants. The basic difference in pretreatment between processes II and III is in the relative amount of total dissolved solids removed by the pretreatment process. The reverse osmosis in process III would remove 90 to 95 percent of the total dissolved solids, and the softening in process II would remove a maximum of only 60 percent of the hardness and an average of about 30 percent of the total dissolved solids. Reverse osmosis produces a much higher quality water than lime-softening units, making the demineralization that follows much more efficient and inexpensive. The lime-softening process produces substantial amounts of sludge, increasing the cost of its disposal. On the basis of both cost and operational criteria, process III was preferred to process II.

A capital cost analysis[71] indicated that processes I (ion exchange only) and III were quite similar (see Tables 21 and 22). A straight ion exchange system is preferred for smaller installations. It was determined that operating costs for process I would be somewhat higher than for process III. On an overall annual cost basis, which included capital depreciation and operation and maintenance costs, process III, consisting of reverse osmosis followed by an ion exchange polishing step, was judged to be the most economically sound method for boiler makeup water treatment.

Depending on the source of boiler makeup water, which could be the city water supply, well water at the plant site, or surface waters, the quality of feedwater to a reverse osmosis-ion exchange system might differ significantly from one source to another. Suspended solids and organic matter may be more significant in the surface water than in ground water,

TABLE 21. COST COMPARISONS OF THREE PROCESSES

Item	Capital cost ($) process for I	II	III
Chemical feed systems	5,000	-	7,000
Filters, 5 to 10 μm	-	-	6,000
Reverse osmosis units (incl. pumps)	-	-	220,000
Lime softener	-	80,000	-
Prefilters	10,000	10,000	10,000
Carbon filters	12,000	-	-
Degasifier	10,000	10,000	10,000
Pumps	31,000	22,000	17,000
Demineralizer system	340,000	280,000	200,000
Water storage	60,000	60,000	60,000
Subtotals	468,000	462,000	530,000
Contingency and technical direction of installation (10%)	46,000	46,000	53,000
Total capital costs	514,000	508,000	583,000
Chemical feed	637	-	5,169
Cartridge replacements, 5 to 10 μm	-	-	1,682
Power for high-pressure pumping	-	-	6,216
Reverse osmosis membrane service contract	-	-	22,075
Lime softening	-	5,886	-
Other power requirements	1,460	1,300	960
Demineralizer regeneration chemicals	78,489	58,867	5,886
Demineralizer resin replacement	17,659	14,716	5,886
Operation labor	14,600	23,725	10,950
Total operating costs	112,845	104,494	58,824
Present worth of operating costs	1,867,600	1,729,391	973,546
Comparative cost	2,381,600	2,237,391	1,556,546
Overall unit cost, $/1000 gal.	1.33	1.26	0.96

Source: Skrinde, R. T., W. M. Steeves, L. S. Shields, and T. L. Tang. Economic and Technical Evaluation of Reverse Osmosis for Industrial Water Demineralization. Paper presented at Industrial Water and Pollution Conference and Exposition, Chicago, Illinois, March 14-16, 1973.

TABLE 22. BASIS OF CALCULATIONS FOR TABLE 21

Lime softening	\$4.00/100,000 gal
Demineralizer series regeneration	
Alternate 1	\$4.00/100,000 gal
Alternate 2	\$40.00/100,000 gal
Alternate 3	\$53.33/100,000 gal
Demineralizer resin regeneration	
Alternate 1	\$4.00/100,000 gal
Alternate 2	\$10.00/100,000 gal
Alternate 3	\$12.00/100,000 gal
Energy	\$0.0061/kWh
Chemicals	
H_2SO_4	\$0.02/lb
NaOH	\$0.04/lb
Na_2SO_3	\$0.08/lb
Polyphosphate	\$0.16/lb
Filter cartridge replacement, 5 to 10 μm	\$1.00/100,000 gal
Reverse osmosis membrane replacement	\$15.00/100,000 gal
Operation labor	\$10.00/h
Alternate 1	3.0 man-hours/day
Alternate 2	6.5 man-hours/day
Alternate 3	4.0 man-hours/day
General maintenance	Not included
Operating cost escalation (compounded annually)	5%
Annual interest rate used for calculating present work of operating costs	10%
Bond redemption period	30 years

Source: Skrinde, R. T., W. M. Steeves, L. S. Shields, and T. L. Tang. Economic and Technical Evaluation of Reverse Osmosis for Industrial Water Demineralization. Paper presented at Industrial Water and Pollution Conf. and Exposition, Chicago, Illinois, March 14-16, 1973.

and on the other hand, the concentration of total dissolved solids may be much higher in some well waters than in the waters of streams and lakes. In general, a filtration system (such as a dual-media filter) is needed to remove the suspended solids, followed by a carbon bed for removing the residual suspended solids, organic materials, and chlorine. Chlorine is harmful to some membranes. Antiscalant addition, pH control, and cartridge filters are also common pretreatment needs.

After reverse osmosis, degasifiers generally are used to remove the carbon dioxide to relieve the burden to the anion-ion exchange units.

Cost comparisons between the system of ion exchange only and the combination of reverse osmosis and ion exchange are shown in Table 23 for the Burbank Public Service Department in California.[70]

Truby[72] reported a cost comparison of a boiler feedwater treatment system with ion exchange only and with a combination of reverse osmosis and ion exchange, as shown in Table 24.

Table 25 compares condensate makeup costs with and without a reverse osmosis unit.

Skrinde et al.[71] compared costs for three processes. Table 21 shows the calculated costs based on criteria shown in Table 22 for a 240-gal/min boiler makeup water treatment system. The overall unit cost is $0.96 per thousand gallons of product water for the recommended reverse osmosis-ion exchange combination systems, which is lower than the cost for two other processes.

RECOMMENDATIONS

Reverse osmosis is a proven technology for removing the bulk of the dissolved solids loading before polishing demineralizers. Its use reduces the total discharge of dissolved solids since little chemical treatment need be used. Presently it is economically attractive to use reverse osmosis for feedwaters with dissolved solids concentrations above 250 to 500 ppm. If penalties were charged for discharging dissolved solids, reverse osmosis would be attractive for feedwaters with lower concentrations.

TABLE 23. RESULTS OF THE BURBANK PUBLIC SERVICE DEPARTMENT COMPARISON AND ANALYSIS OF OPERATING COSTS OF DEMINERALIZER AND REVERSE OSMOSIS SYSTEMS

Cost element	Operating history	
	May-June 1970	May-June 1971
Demineralizer, 36-in. diam.		
Product water, gal	746,300	862,857
Regenerations	67	28
Operating labor (1 hr/regeneration), $	361	151
Chemicals, $	781	326
Demineralizer, 30-in. diam.[a]		
Product water, gal	35,790	266,000
Regenerations	6	6
Operating labor (1 hr/regeneration), $	32	32
Chemicals, $	38	38
Feedwater cost ($53/acre-ft), $	127	40[b]
Regeneration water		
Quantity, gal	236,000	118,000
Cost, $	39	19
Reverse osmosis system		
Operating labor (1 hr/day), $		328
Electric power ($1.20/day), $		73
Chemicals ($0.29/day), $		18
Feedwater cost ($53/acre-ft), $		233
Total cost, $	1378	1258
Cost/1000 gal deionized water, $	1.77	1.16

[a] Only in operation when 36-in.-diameter unit is being regenerated.

[b] Not all product water flows through the reverse osmosis system before deionization; some raw water is mixed with the reverse osmosis product before the demineralizer because maximum reverse osmosis system throughput is less than the makeup requirements.

Source: Rowland, H., I. Nasbaum, and F. J. Jester. Consider Reverse Osmosis for Producing Feedwater. Power, December 1971. Reprinted with permission from Power Magazine. Copyright McGraw-Hill, Inc., 1971.

TABLE 24. COST COMPARISON OF A BOILER FEEDWATER TREATMENT SYSTEM WITH ION EXCHANGE ONLY AND WITH A COMBINATION OF REVERSE OSMOSIS AND ION EXCHANGE

Cost item[a]	Ion exchange only ($/yr)	Ion exchange only ($/1000 gal)	Combination of reverse osmosis and ion exchange ($/yr)	Combination of reverse osmosis and ion exchange ($/1000 gal)
Capital	160,230	1.015	168,430	1.067
Labor	96,000	0.608	96,000	0.608
Maintenance	50,000	0.317	50,000	0.317
Pretreatment chemicals	46,460	0.294	46,440	0.294
Demineralization chemicals	172,680	1.094	15,880	0.101
Resin	32,310	0.205	8,950	0.057
Modules	-	-	30,880	0.196
Waste chemicals	81,300	0.515	2,570	0.016
Energy	12,430	0.079	40,270	0.255
Total	651,410	4.13	459,420	2.91

[a] Cost based on water containing 960 mg/ℓ total dissolved solids.

Source: Truby, R. Reverse Osmosis for Boiler Feedwater Treatment. Power Engineering, December 1976. Reprinted by permission.

TABLE 25. COMPARISON OF CONDENSATE MAKEUP COSTS
WITH AND WITHOUT REVERSE OSMOSIS UNIT

Without reverse osmosis

Pretreatment
Cation-anion makeup demineralizer
(estimated 40,000-gal service run)
Mixed-bed makeup demineralizer

One year's operation, 1.5 x 10^7 gal $83,700

With reverse osmosis (2-yr old membranes)

Pretreatment
Operating membrane (replacement every 2 years)
Cation-anion makeup demineralizer
(200,000-gal service run)
Mixed-bed makeup demineralizer

One year's operation, 1.5 x 10^7 gal $25,200

With reverse osmosis (new membranes)

Pretreatment
Operating membrane (replacement every 2 years)
Cation-anion makeup demineralizer
(1,000,000-gal service run)
Mixed-bed makeup demineralizer

One year's operation, 1.5 x 10^7 gal $12,000

Source: Wadlington, M. Chemical Regenerant Savings Can Pay for a Reverse Osmosis Unit. Industrial Water Engineering, June-July 1976. Reprinted by permisssion.

SECTION 10

BOILER BLOWDOWN

CHARACTERISTICS OF WASTEWATER

The quantity of boiler blowdown varies with allowable boiler water solids content, condenser leakage, makeup water quality, and boiler operating conditions. Old plants operating at low pressures can tolerate concentrations of total dissolved solids in boiler water as high as 2500 mg/ℓ, with an average blowdown rate of 10 percent. Modern boilers can operate with concentrations of total dissolved solids of less than 50 mg/ℓ, which will have a blowdown range of 0.1 to 1 percent of steamflow, or about 20 to 200 gpd/MW. The chemical characteristics of boiler blowdown depend on the construction materials, the feedwater chemical control program, and the type of plant operation. Generally, the boiler blowdown has a basic pH, a low concentration of total dissolved solids, and very small amounts of copper, iron, nickel, and chromium; it can be reused in other operations of the power plant with or without treatment.[32]

According to a TVA study,[25] boiler design pressure has the most significant effect on the quality of boiler feedwater, condensate, and blowdown. Scale of calcium and magnesium salts and deposits of iron oxide, elemental copper, and copper oxide are frequently found in boilers, even when operating with very pure feedwater. Chemicals such as sodium phosphates, EDTA, and NTA are used to prevent these salts from precipitating on boiler surfaces. To prevent corrosion, boiler water must be neutralized with alkalies such as sodium carbonate, sodium hydroxide, or ammonia. Chemical deoxygenation is commonly used to prevent corrosion of metallic surfaces.

The quantities of ammonia, phosphate, iron, and copper in boiler blowdown may be significant,[26] depending on the kind of chemical additives and the type of boiler used.

ALTERNATIVE TREATMENTS

Normally (for modern high pressure boilers) the quality of boiler blowdown is better than that of the raw makeup water supply. Thus, the blowdown is recycled back to the inlet to the makeup water treatment system, which could use the reverse osmosis-ion exchange combination process as mentioned in Section 9. The blowdown from a low-pressure, drum-type boiler generally contains higher concentrations of total dissolved solids and can be discharged into neutral and alkaline ash ponds to precipitate iron and copper. This technique is being practiced by TVA. For those power plants with acidic ash ponds or where the ash is dry-handled, the boiler blowdown has to be treated with other methods. To achieve the goal of water reuse, the lower quality blowdown can be treated by a reverse osmosis-ion exchange boiler makeup treatment system with equal or higher cost-effectiveness than that for the high-pressure boiler blowdown.

The pretreatment needed generally includes pH control (lowering the pH by adding H_2SO_4), antiscalent addition (sodium hexametaphosphate), and cartridge filtration. Degasifier and ion exchange units may be needed to treat the product water from the reverse osmosis system before it is reused as the boiler makeup water.

The process recommended for boiler blowdown treatment is essentially similar to the boiler makeup water treatment system proposed in Section 9, except that the prefilters (such as dual-media filters) are excluded. Cost should be similar to those discussed in the section on boiler makeup water.

RECOMMENDATIONS

Boiler blowdown can be returned to the boiler makeup water treatment system, which may use reverse osmosis as a roughing demineralizer.

SECTION 11

CHEMICAL CLEANING WASTES

CHARACTERISTICS OF WASTEWATER

Periodic cleaning of metal surfaces in steam generators is required to remove the accumulated deposits, which raise water wall temperatures, reduce heat transfer, and lower cycle efficiency. A wide range of cleaning compounds and neutralizing agents is used. The frequency of cleaning and the quantity and quality of pollutants discharged depend on plant reliability requirements, construction materials, use of corrosion inhibitors, antifoulants, and biocides, compliance with equipment and water quality control requirements, and mode of operation of unit and equipment. Required cleaning frequencies for various equipment and the corresponding waste volume are typified in Table 26.[32]

Metal cleaning processes used by TVA are either circulation or soaking methods. Waste streams from the circulation method consist of (1) an acid waste in which the iron is chelated with cleaning solvent such as citric acid or hydroxyacetic-formic acid and (2) a passivation drain. Waste streams from the soaking method consist of (1) an acid waste in which the iron is not chelated with cleaning solvent such as hydrochloric acid, (2) an alkaline copper waste in which the copper is strongly complexed with ammonia, and (3) a passivation drain. Waste solutions from these processes contain large amounts of metallic species, nitrogen and phosphate compounds, and organic materials. The characteristics of the chemical cleaning wastes depend on the method of cleaning, type of boiler and accessory equipment cleaned, and the types of cleaning chemicals. Characteristics of the wastes resulting from cleaning processes at several TVA plants are presented in Tables 27, 28, and 29. Characteristics of the wastes for cleanings at the same plant may vary. The volume of wastewater resulting from cleaning processes at TVA plants ranges from about 0.3 to 0.9 x 10^6 gal per unit per cleaning.[73]

ALTERNATIVE TREATMENTS

Results of a recent study conducted by TVA showed that the acid- and neutralization-phase cleaning wastes can be treated to meet the effluent limitation guidelines (1 mg/ℓ copper and 1 mg/ℓ iron) by a conventional chemical precipitation process. Treatment of the alkaline-phase cleaning waste is complicated by the strong copper-ammonia complexes.

TABLE 26. TYPICAL PLANT EQUIPMENT WHICH MAY REQUIRE PERIODIC CLEANING

Equipment	Materials	Waste volume per cleaning or wash (gal/MW)	Typical frequency per year
Boiler, steam generators	Stainless steel Carbon steel Inconel	50-400	0.2-1
Feedwater heaters	Carbon steel Stainless steel Admiralty brass 90/10, 80/10, 70/10 Cu-Ni Monel Arsenical copper		Only preoperational
Condenser tubes	Admiralty brass 90/10 Cu-Ni Stainless steel		
Air preheaters	Carbon steel	100-1500	4-24
Boiler fireside		100-1000	2-8
Miscellaneous equipment, piping	Carbon steel Stainless steel Copper alloys		

Source: Wright, J. H., and S. J. Dea. Water Pollution Control in the Power Generation Industry. Industrial Wastewater Management Handbook, ed. H. S. Azad, Copyright McGraw-Hill, 1976. Reprinted by permission from McGraw-Hill Book Company.

TABLE 27. CHARACTERISTICS OF CHEMICAL CLEANING WASTEWATER--ACID PHASE COMPOSITE

		Plant						
Constituent	Unit	A[a]	A[c]	C[b]	G[b]	I[b]	K[b]	L[b]
Waste Volume	millions of gallons	0.175-0.250	0.175-0.250	0.217	0.099	0.087	0.070	0.090
pH	units	3.3	10.1	0.8	0.7	0.7	0.5	0.7
Suspended solids	mg/ℓ	57	51	8	120	18	35	33
Total organic carbon	mg/ℓ	4600	10000	240	90	1800	220	120
Chemical oxygen demand	mg/ℓ	9900	16000	1200	1500	1200	1900	1500
Oil & grease	mg/ℓ	23	16	<5	11	7.6	20	23
Phenols	mg/ℓ	0.050	0.013	0.065	0.070	0.035	0.020	0.025
Silica	mg/ℓ	19	-	66	120	240	31	-
Ammonia nitrogen	mg/ℓ	325	6200	140	80	220	290	150
Organic nitrogen	mg/ℓ	225	6400	0.06	140	75	10	870
Nitrate & nitrite nitrogen	mg/ℓ	-	49	0.07	<0.01	<0.01	<0.01	-
Phosphorus	mg/ℓ	1.2	1.1	30	50	35	50	45
Sulfate	mg/ℓ	-	<4	<1	10	<1	<1	-
Aluminum	mg/ℓ	-	1.8	6.5	6.6	7.0	8.2	-
Arsenic	mg/ℓ	0.008	0.41	0.060	0.010	0.030	0.055	0.035
Barium	mg/ℓ	-	0.2	<0.1	0.4	0.1	0.3	-
Beryllium	mg/ℓ	-	<0.01	<0.01	<0.01	<0.01	<0.01	-
Cadmium	mg/ℓ	<0.001	0.12	0.010	0.051	0.032	<0.10	0.001
Calcium	mg/ℓ	16	20	42	70	53	64	74
Chromium	mg/ℓ	<0.005	15	1.5	6	1.1	<8.3	0.005
Copper	mg/ℓ	0.69	0.7	2.2	7.6	18	13	47
Iron, total	mg/ℓ	4200	4800	1300	3820	1420	3720	2780
Lead	mg/ℓ	-	1.1	0.4	3.8	0.86	5.2	<0.010
Magnesium	mg/ℓ	-	1.6	8.7	6.5	5.7	8.8	-
Manganese	mg/ℓ	19	37	6.9	29	10	28	22
Mercury	mg/ℓ	-	<0.0004	<0.0002	<0.0002	0.0002	0.0002	-
Nickel	mg/ℓ	110	8.3	77	260	170	300	150
Potassium	mg/ℓ	-	3.1	1.4	2.3	1.5	1.8	-
Selenium	mg/ℓ	-	<0.008	<0.004	<0.002	<0.002	<0.002	-
Silver	mg/ℓ	-	0.03	0.02	0.02	0.07	0.03	-
Sodium	mg/ℓ	-	840	31	74	40	49	-
Tin	mg/ℓ	-	1.5	<1	7.3	<1	2.8	-
Zinc	mg/ℓ	0.94	2.5	5.9	170	34	53	24
Iron, ferrous	mg/ℓ	-	4800	-	-	-	-	-

[a] Circulation method with hydroxyacetic-formic acid.

[b] Soaking method with hydrochloric acid.

[c] Circulation method with citric acid followed by addition of NH_4OH.

Source: Steiner, G. R., C. L. McEntyre, and T.-Y. J. Chu. Treatment of Metal Cleaning Wastes at TVA Power Plants. Paper presented at 84th National Meeting of American Institute of Chemical Engineers, Atlanta, Georgia, February 26-March 1, 1978. 44 pp.

TABLE 28. CHARACTERISTICS OF CHEMICAL CLEANING WASTEWATER-- ALKALINE PHASE COMPOSITE

Constituent	Unit	Plant				
		C	G	I	K	L
Waste Volume	millions of gallons	0.217	0.165	0.116	0.140	0.120
Dissolved solids	mg/ℓ	340	1400	1400	1900	1600
Suspended solids	mg/ℓ	8	71	47	200	7
Chemical oxygen demand	mg/ℓ	24	120	61	84	160
Oil & grease	mg/ℓ	<5	<5	<5	<5	-
Silica	mg/ℓ	7.2	14	50	13	-
Ammonia nitrogen	mg/ℓ	700	2000	2100	4200	4700
Organic nitrogen	mg/ℓ	40	<10	270	2600	3600
Nitrate & nitrite nitrogen	mg/ℓ	0.04	0.51	0.21	0.46	-
Phosphorus	mg/ℓ	10	30	2.0	400	275
Bromide	mg/ℓ	52	<5	-	-	<5
Chloride	mg/ℓ	60	-	350	110	180
Fluoride	mg/ℓ	1.5	6.1	6	5.6	-
Sulfate	mg/ℓ	<1	<1	<1	18	-
Aluminum	mg/ℓ	<0.2	<0.2	0.4	0.3	-
Arsenic	mg/ℓ	0.048	<0.005	0.012	<0.010	0.030
Barium	mg/ℓ	<0.1	<0.1	<0.1	<0.1	-
Beryllium	mg/ℓ	<0.01	<0.01	<0.01	<0.01	-
Cadmium	mg/ℓ	<0.001	<0.001	<0.001	<0.001	-
Calcium	mg/ℓ	3.0	0.4	<1.0	4.9	-
Chromium	mg/ℓ	<0.005	<0.005	<0.005	<0.005	-
Copper	mg/ℓ	100	790	510	680	590
Iron	mg/ℓ	1.7	4.9	2.9	2.2	<0.05
Lead	mg/ℓ	<0.010	<0.010	<0.010	<0.010	-
Magnesium	mg/ℓ	2.9	0.67	0.1	0.51	-
Manganese	mg/ℓ	0.03	0.04	0.03	0.05	-
Mercury	mg/ℓ	<0.0002	<0.0002	0.0006	0.0006	-
Nickel	mg/ℓ	0.52	2.5	0.94	3.3	0.62
Potassium	mg/ℓ	70	220	<0.1	230	260
Selenium	mg/ℓ	<0.002	<0.002	<0.002	<0.002	-
Silver	mg/ℓ	<0.01	0.02	<0.01	0.04	-
Sodium	mg/ℓ	3.7	15	0.1	12	-
Tin	mg/ℓ	<1	<1	<1	<1	-
Zinc	mg/ℓ	0.06	0.54	0.17	0.35	0.19

Source: Steiner, G. R., C. L. McEntyre, and T.-Y. J. Chu. Treatment of Metal Cleaning Wastes at TVA Power Plants. Paper presented at 84th National Meeting of American Institute of Chemical Engineers, Atlanta, Georgia, February 26-March 1, 1978. 44 pp.

TABLE 29. CHARACTERISTICS OF CHEMICAL CLEANING WASTEWATER--PASSIVATION DRAIN

Constituent	Unit	Plant[a]					
		A	C	G	I	K	L
Waste volume	millions of gallons	0.110	0.072	0.033	0.029	0.035	0.030
pH	units	9.5	11.9	12.2	12.0	10.7	11.9
Dissolved solids	mg/ℓ	70	4000	4500	5400	2500	5300
Suspended solids	mg/ℓ	10	88	140	20	10	12
Chemical oxygen demand	mg/ℓ	92	68	68	46	68	76
Oil & grease	mg/ℓ	<5	-	<5	-		<5
Ammonia nitrogen	mg/ℓ	80	3.2	12	22	21	32
Organic nitrogen	mg/ℓ	110	4.3	5	38	5	<0.00
Nitrate & nitrite nitrogen	mg/ℓ	-	<0.01	0.03	0.50	0.01	0.03
Phosphorus	mg/ℓ	-	-	770	850	420	980
Copper	mg/ℓ	0.13	0.65	25	1.7	0.4	2.8
Iron	mg/ℓ	4.6	3.2	28	4.4	2.3	1.3
Sodium	mg/ℓ	-	150	1800	1.3	960	2400
Hydrazine	mg/ℓ	0.025	-	-	-	-	0.001

[a] Plant A uses circulation method; all other plants use soaking method.

Source: Steiner, G. R., C. L. McEntyre, and T.-Y. J. Chu. Treatment of Metal Cleaning Wastes at TVA Power Plants. Paper presented at 84th National Meeting of American Institute of Chemical Engineers, Atlanta, Georgia, February 26-March 1, 1978. 44 pp.

Treatment of hydrochloric acid cleaning wastes from TVA plants[73] by adding lime to reach a pH of about 10 decreased the concentration of dissolved iron to less than 1.0 mg/ℓ. It also removed the lower concentrations of copper (2.2 to 47 mg/ℓ) present in the waste to 1.0 mg/ℓ. In a similar study, hydroxyacetic-formic acid wastes were treated with lime. The concentration of dissolved iron reached 1.0 mg/ℓ at pH 10.1 and 0.33 mg/ℓ at pH 12.0. Citric acid wastes were treated with hydrogen peroxide followed by pH adjustment to 13.0 with caustic soda, which reduced the dissolved iron concentrations to below 1.0 mg/ℓ. Waste from the acid stages of the chemical cleaning process can be treated in an alkaline ash pond that has a pH of about 9, where the high concentrations of iron in the wastes will precipitate and the dissolved iron can be reduced to an "equivalent" concentration of 1.0 mg/ℓ in which the dilution factor is excluded.

The theoretical minimum solubility for copper hydroxides occurs at pH values of about 8.9 with a resulting dissolved copper concentration of 0.004 mg/ℓ. However, adjustment of alkaline cleaning waste to this pH does not reduce the dissolved copper in the waste to less than 1.0 mg/ℓ because the copper is complexed with ammonia.[73] Copper will be removed from solution to levels less than 1.0 mg/ℓ if the copper-ammonia complex is broken and the waste is still alkaline. Treatment of alkaline wastes containing 730 mg/ℓ of copper and 27,000 mg/ℓ of ammonia nitrogen with sodium sulfide reduces the dissolved copper level to below 1.0 mg/ℓ. However, contact of any acid with sodium sulfide produces hydrogen sulfide gas. If the pH of the waste is adjusted to below 9.0, the residual sulfide in the waste would be converted to hydrogen sulfide. Due to the potential safety hazard from hydrogen sulfide, treatment of alkaline wastes with sodium sulfide is not recommended.[73] Studies with lime and caustic soda treatment indicated that the concentration of dissolved copper in the alkaline chemical cleaning wastes can be reduced to 1.0 mg/ℓ if the pH of the wastes is raised to a value of 11.5 to 12.0 and sufficient reaction time is allowed. Agitation of the wastes by circulation or aeration at high pH values speeds removal of ammonia, which, in turn, accelerates removal of dissolved copper.[73] The ion exchange process has also been tried to treat the alkaline chemical cleaning wastes. It was found to be impractical because of the low breakthrough capacity and low regeneration efficiency of the resins, which would not provide cost-effective treatment of the wastes.[73] Studies on treating the alkaline chemical cleaning wastes in TVA ash ponds showed that the chelated copper-ammonia bonds can be broken by dilution with ash pond water, which allows precipitation of the copper at alkaline pH values. Additional copper is removed by adsorption on fly ash. A detention time of up to 10 hours is required for breaking the copper-ammonia bond and for subsequent chemical precipitation of the copper.[74]

Reverse Osmosis

Studies by TVA on treating chemical cleaning wastes by reverse osmosis, especially the alkaline wastes, were begun because the metal ions, especially copper, in their complex forms are difficult to reduce to the level required by the EPA guidelines with conventional chemical treatment processes. TVA also hoped to meet the goal of water conservation by treatment and reuse of the overall chemical cleaning wastes.

The alkaline-phase drain cleaning waste generally has a pH of 9 to 12. Experiments were conducted using DuPont hollow-fiber and DuPont spiral-wound modules to treat straight alkaline wastes and Roga spiral-wound, Dow hollow-fiber, and Fluid Science tubular modules to treat neutralized wastes. All alkaline and neutralized wastes were filtered through 1- to 3-μm fiber filters to remove suspended solids before the membrane tests. During the neutralization process, the waste was first adjusted with 36 N hydrochloric acid to a pH of 6.0, where some copper precipitates; it was then filtered and readjusted to a pH of 4.0. Results of chemical cleaning waste treatment studies shown in Table 30 indicate that cellulose acetate membrane modules have poorer rejection on copper complex and total dissolved solids than do polyamide membrane modules, but all membranes have poor rejection on total ammonia. The DuPont hollow-fiber module appears most promising. The studies showed that the polyamide membranes are able to treat the waste under conditions of low volume recovery. However, it would be economically desirable to maximize recovery. Therefore, the DuPont modules were selected to treat the alkaline-phase cleaning waste for high volume recovery. The membrane fouling problems resulting from the copper precipitates in the unstable cleaning waste were considered a possible key factor preventing the operation at the high volume recovery. However, the membrane processes were still considered practicable if a simple and inexpensive pretreatment process could be found for this waste. To investigate this possibility, a study was conducted to neutralize the alkaline-phase cleaning waste with acid-phase cleaning waste to a pH of 6. After a settling process, the clarified solution was treated by ultrafiltration to remove the residual fine particles. Then the ultrafiltration permeate was adjusted to a pH of 5 by hydrocloric acid addition before treatment by reverse osmosis.

The characteristics of composite alkaline-phase cleaning waste (drain plus flush) used for this study is shown in Table 31. A pH of 6 or more is necessary for precipitation of iron from the cleaning wastes to meet the effluent limits, but the neutralization process cannot remove copper to the required 1-mg/ℓ concentration. Therefore, the combined treatment of acid- and alkaline-phase cleaning wastes was considered as an effective pretreatment process to reduce the strength of the wastes and to remove iron (from the acid-phase cleaning wastes) before the membrane processes. After the sludge settling, the clarified solutions were treated by ultrafiltration (Union Carbide 3NJR module) for colloidal particle removal.

The test results are shown in Table 32. The ultrafiltration permeates were then adjusted to a pH of 5 by adding hydrochloric acid. These pretreated boiler cleaning wastes were treated by three spiral-wound reverse osmosis membranes--DuPont, UOP-ROGA, and Osmonics. The test results are presented in Tables 33, 34, and 35.

TABLE 30. RESULTS OF REVERSE OSMOSIS STUDIES ON CHEMICAL CLEANING WASTES

Membrane type	Feed composition	Flux (gal/min)	Rejection[a] (%)	Pressure (psig)	Feedflow (gal/min)
DuPont Hollow Fiber	Alkaline copper waste Cu, 2200 mg/ℓ NH_3-N, 10,500 mg/ℓ TDS, 4500 mg/ℓ pH, 11.1	0.85	Cu, 99.98 NH_3-N, 20.39 TDS, 95.84	350	4.2
DuPont Spiral Wound	Alkaline copper waste Cu, 1700 mg/ℓ NH_3-N, 9450 mg/ℓ TDS, 4300 mg/ℓ pH, 10.0	0.30	Cu, 98.82 NH_3-N, 40.74 TDS, 87.44	400	3.8
Roga Spiral Wound	Neutralized copper waste Cu, 820 mg/ℓ NH_3-N, 4100 mg/ℓ TDS, 2600 mg/ℓ pH, 4.35	0.35	Cu, 83.62 NH_3-N, 58.8 TDS, 79.04	400	4.15
UOP Fluid Science Tubular	Neutralized copper waste Cu, 2000 mg/ℓ pH, 4.0	0.06	Cu, 78.45	550	3.75
Dow Hollow Fiber	Neutralized copper waste Cu, 410 mg/ℓ pH, 4.0	0.01	Cu, 74.95	200	4.1

[a] Rejection = 1 - (concentration in permeate)/(concentration in feed).

TABLE 31. CHARACTERISTICS OF COMPOSITE ALKALINE-PHASE CLEANING WASTE[a]

Constituent	Concentration[b]
pH	10.6
Dissolved solids	1200
Suspended solids	10
Total organic carbon	400
Chemical oxygen demand	50
Oil and grease	3
Silica	10
Ammonia nitrogen	2900
Organic nitrogen	1435
Nitrite and nitrate nitrogen	0.6
Phosphorus	1
Antimony	0.1
Bromide	53
Chloride	63
Fluoride	1
Sulfate	-
Aluminum	<0.2
Arsenic	0.016
Barium	<0.1
Beryllium	<0.01
Cadmium	<0.001
Calcium	<1
Chromium	0.01
Copper	313
Iron	0.3
Lead	<0.01
Magnesium	0.3
Manganese	0.01
Mercury	<0.0002
Nickel	0.6
Potassium	173
Selenium	<0.001
Silver	0.07
Sodium	1
Tin	<1
Zinc	7

[a] One drain plus two flushes.

[b] All values in milligrams per liter except pH which is in units.

TABLE 32. PERFORMANCE OF UNION CARBIDE 3NJR ULTRAFILTRATION MODULE IN POLISHING SUSPENDED SOLIDS FROM THE PRETREATED BOILER CLEANING WASTES

Volume recovery[a]	Suspended solids concentrations (mg/ℓ) in Feed	Suspended solids concentrations (mg/ℓ) in Permeate
0.01	6	2
0.5	9	2
0.95	57	3

[a] V_p/V_F, where V_p = volume of permeate and V_F = initial volume of feed solution.

Tables 27 through 31 show that the suspended solids in the chemical cleaning wastes vary from 7 to 200 mg/ℓ. Before feeding into the membrane system, these wastes were treated by settling, with or without chemical assistance, followed by filtration such as dual-media filtration, pH control, antiscalent addition, and cartridge filters. Depending on the type of reuse, chemical cleaning wastes which have been treated by reverse osmosis may or may not need further treatment.

Cost Estimates

Literature information is unavailable on cost for the membrane process of treating power plant chemical cleaning wastes. To determine the magnitude of treatment costs, the cost of treating other industrial wastes, which have been studied extensively in both technical and economic terms and which have similar wastewater characteristics as those of chemical cleaning wastes, were sought.

The wastewaters from the plating industry possess various metal ions, acid, caustic, and other chemical ingredients such as cyanides and phenols, which are also the constituents of the chemical cleaning wastes. The concentrations of each individual constituent may differ, but the occurrences of the constituents, as a group, are quite compatible, except that generally the chemical cleaning wastes have much higher concentrations of suspended solids than do the plating wastes.

Golomb[75] studied closed-loop reverse osmosis treatment of nickel-plating solutions and projected cost estimates (Table 36). Three levels of operation with dragout rates of 15, 50, and 500 gpd were considered. A flux rate of 10.7 gal/(ft^2·day) at 450 psi pressure was used. Capital costs were based on straight-line amortization over a 5-year period at an interest rate of 8.5 percent. Operation was assumed for 240 days per year, with three 8-hour shifts per day. Operating labor costs of $8.00 per hour and a membrane life of 18 months were assumed. Total operating and maintenance costs per thousand gallons of permeate are shown in Table 37.

TABLE 33. PERFORMANCE OF DUPONT SPIRAL-WOUND REVERSE OSMOSIS MODULE IN TREATING PRETREATED BOILER CLEANING WASTES[a], [b]

Constituent	$V_p/V_F = 0.01$		$V_p/V_F = 0.125$		$V_p/V_F = 0.25$		$V_p/V_F = 0.375$		$V_p/V_F = 0.5$		$V_p/V_F = 0.95$	
	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate
Permeate flow, gal/min	-	0.24	-	0.22	-	0.21	-	0.18	-	0.16	-	0.14
Feed temperature, °C	26.2	-	26.2	-	-	-	-	-	-	-	-	-
pH, units	5.01	5.49	-	-	-	-	-	-	4.91	5.41	4.90	5.35
Conductivity, μmhos/cm	20,100	2510	-	-	-	-	-	-	25,200	3300	29,200	4400
NH_3-N, mg/ℓ	2400	160	2200	180	2400	280	-	-	3700	440	4800	620
Org.-N, mg/ℓ	1700	540	-	-	-	-	-	-	-	-	2400	580
TOC, mg/ℓ	25	5.2	-	-	-	-	-	-	35	6.2	35	7.4
COD, mg/ℓ	220	47	-	-	-	-	-	-	430	52	530	92
SiO_2, mg/ℓ	6.5	0.3	-	-	9.5	0.1	-	-	18	0.4	23	0.6
PO_4-P, mg/ℓ	0.23	0.02	-	-	-	-	-	-	-	-	0.1	0.02
Cl, mg/ℓ	4000	-	920	-	-	-	-	-	-	-	8400	1500
SO_4, mg/ℓ	1	<1	-	-	-	-	-	-	-	-	1	<1
F, mg/ℓ	110	22.5	-	-	-	-	-	-	-	-	150	70
Ca, mg/ℓ	45	3.2	-	-	-	-	-	-	-	-	76	5.9
Mg, mg/ℓ	4.1	0.8	-	-	-	-	-	-	-	-	12	1.0
Na, mg/ℓ	9.5	0.5	-	-	-	-	-	-	-	-	14.2	2.1
Br, mg/ℓ	2.2	0.2	-	-	-	-	-	-	-	-	13	0.7
BrO_3, mg/ℓ	14	0.4	-	-	-	-	-	-	20	1.6	26	2.4
Ag, mg/ℓ	0.06	<0.01	-	-	-	-	-	-	-	-	0.1	<0.01
As, mg/ℓ	<0.002	<0.002	-	-	-	-	-	-	-	-	0.003	<0.002
Ba, mg/ℓ	0.7	<0.01	-	-	-	-	-	-	-	-	-	-
Cr, mg/ℓ	<0.005	<0.005	-	-	-	-	-	-	-	-	0.13	0.011
Cu, mg/ℓ	36	1.8	36	2.0	41	2.5	-	-	50	4.0	72	5.4
Fe, mg/ℓ	0.62	0.07	-	-	-	-	-	-	2.6	0.19	7.7	0.37
K, mg/ℓ	120	11	-	-	-	-	-	-	190	23	270	28
Ni, mg/ℓ	30	1.8	-	-	-	-	-	-	-	-	110	4.9
Zn, mg/ℓ	7.2	0.45	-	-	-	-	-	-	15	1.1	18	1.4

[a] Operation pressure = 400 psig; feedflow rate = 3.9 gal/min; V_p = volume of permeate; V_F = initial volume of feed solution.

[b] Dashes indicate no data is available.

TABLE 34. PERFORMANCE OF UOP-ROGA 4100 SPIRAL-WOUND REVERSE OSMOSIS MODULE IN TREATING PRETREATED BOILER CLEANING WASTES[a,b,c]

Constituent	V_p/V_F = 0.01		V_p/V_F = 0.125		V_p/V_F = 0.25		V_p/V_F = 0.375		V_p/V_F = 0.05		V_p/V_F = 0.625		V_p/V_F = 0.75		V_p/V_F = 0.875		V_p/V_F = 0.95	
	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate
Permeate flow, gal/min	-	1.07	-	1.01	-	0.96	-	0.93	-	0.89	-	0.84	-	0.72	-	0.65	-	0.48
Feed temperature, °C	25	-	25.5	-	25.7	-	25.8	-	25.9	-	26	-	26.3	-	27.3	-	-	-
pH, units	5.0	5.1	5.2	-	5.2	5.04	5.2	-	5.2	5.03	5.18	-	5.14	5.13	5.10	-	5.03	5.4
Conductivity, µmhos/cm	11,800	3810	-	-	13,200	4350	-	-	15,600	5450	-	-	20,000	7700	-	-	29,000	15,400
NH_3-N, mg/ℓ	1900	540	1800	700	2200	600	3400	800	3000	650	3200	850	4200	1400	5900	1300	7200	2200
Org.-N, mg/ℓ	1200	90	-	-	-	-	-	-	2700	720	-	-	-	-	-	-	-	-
TOC, mg/ℓ	40	8	-	-	-	-	-	-	50	8	-	-	-	-	-	-	100	17
COD, mg/ℓ	320	120	-	-	-	-	-	-	400	140	-	-	-	-	-	-	-	-
SiO_2, mg/ℓ	11	0.4	-	-	13	0.8	-	-	15	0.7	-	-	16	1.7	-	-	-	-
PO_4-P, mg/ℓ	0.07	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cl, mg/ℓ	9500	1600	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19,000	8600
SO_4, mg/ℓ	<1	<1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6	<1
F, mg/ℓ	88	23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	280	130
Ca, mg/ℓ	15	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	50	7
Mg, mg/ℓ	2.3	0.48	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.9	1.2
Na, mg/ℓ	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	34	6.7
Ag, mg/ℓ	0.07	<0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.09	0.01
As, mg/ℓ	<0.002	<0.002	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba, mg/ℓ	<1	<0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.2	0.3
Cr, mg/ℓ	0.45	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu, mg/ℓ	45	4.6	65	7.2	63	6.4	69	7.6	94	12	98	9	-	-	-	-	210	30
Fe, mg/ℓ	0.37	<0.05	-	-	-	-	-	-	0.54	<0.05	-	-	-	-	-	-	1.7	0.14
K, mg/ℓ	120	25	-	-	-	-	-	-	170	33	-	-	-	-	-	-	500	80
Ni, mg/ℓ	36	3.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	150	13
Zn, mg/ℓ	11	1.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	38	3.7

[a] Two modules in series.

[b] Operation pressure = 400 psig; feedflow rate = 3.9 gal/min; V_p = volume of permeate; V_F = initial volume of feed solution.

[c] Dashes indicate no data is available.

TABLE 35. PERFORMANCE OF OSMONIC P.V. 192-197 SPIRAL-WOUND REVERSE OSMOSIS MODULE IN TREATING PRETREATED BOILER CLEANING WASTES[a,b]

Constituent	$V_p/V_F = 0.01$		$V_p/V_F = 0.125$		$V_p/V_F = 0.25$		$V_p/V_F = 0.375$		$V_p/V_F = 0.5$		$V_p/V_F = 0.625$		$V_p/V_F = 0.75$		$V_p/V_F = 0.875$		$V_p/V_F = 0.95$	
	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate
Permeate flow, gal/min	-	0.12	-	0.12	-	0.11	-	0.10	-	0.10	-	0.08	-	0.07	-	0.06	-	0.05
Feed temperature, °C	23.2	-	25.2	-	26.5	-	27.0	-	27.2	-	27.5	-	28	-	29	-	29	-
pH, units	5.02	5.4	5.2	4.5	5.2	4.52	5.2	4.51	5.3	4.66	5.37	4.62	5.25	4.64	5.19	4.9	5.16	4.75
Conductivity, µmhos/cm	9700	2100	13,600	2090	14,500	2560	14,150	3050	15,400	3600	21,500	4300	25,000	6050	28,000	9000	33,300	11,500
NH_3-N, mg/ℓ	1800	240	2000	280	2600	330	2800	400	3700	420	4200	600	5300	800	6400	-	7500	1800
Org.-N, mg/ℓ	1600	200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2000	420
TOC, mg/ℓ	12	10	-	-	-	-	-	-	55	10	-	-	-	-	-	-	60	15
COD, mg/ℓ	230	560	-	-	-	-	-	-	320	90	-	-	-	-	-	-	1200	350
SiO_2, mg/ℓ	20	0.9	-	-	26	1.0	-	-	19	1.7	-	-	46	3.0	-	-	92	13
PO_4-P, mg/ℓ	0.04	0.02	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15	0.02
Cl, mg/ℓ	4300	580	-	-	-	-	-	-	7100	1400	-	-	-	-	-	-	-	-
SO_4, mg/ℓ	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8	<1
F, mg/ℓ	98	12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	310	50
Ca, mg/ℓ	27	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	37	3.5
Mg, mg/ℓ	3.1	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9	0.1
Na, mg/ℓ	4.3	0.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20	2.1
Br, mg/ℓ	7.7	0.2	-	-	-	-	-	-	29	1.0	-	-	-	-	-	-	87	1.0
BrO_3, mg/ℓ	13	9.6	-	-	-	-	-	-	13	12	-	-	-	-	-	-	32	22
Ag, mg/ℓ	0.02	<0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.11	0.02
As, mg/ℓ	0.004	<0.002	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.004	<0.002
Ba, mg/ℓ	0.54	<0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.2	<0.1
Cr, mg/ℓ	0.053	<0.005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02	<0.005
Cu, mg/ℓ	38	0.58	41	0.58	46	0.68	52	0.74	67	0.99	78	1.4	92	1.8	130	2.7	160	3.9
Fe, mg/ℓ	0.59	0.08	-	-	-	-	-	-	1.4	<0.05	-	-	-	-	-	-	2.4	<0.05
K, mg/ℓ	120	9	-	-	-	-	-	-	230	16	-	-	-	-	-	-	530	61
Ni, mg/ℓ	33	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	180	1.6
Zn, mg/ℓ	7.1	0.09	-	-	-	-	-	-	14	0.17	-	-	-	-	-	-	102	2.1

[a] Operation pressure = 400 psig; feedflow rate = 3.9 gal/min; V_p = volume of permeate; V_F = initial volume of feed solution.

[b] Dashes indicate no data is available.

TABLE 36. SUMMARY OF PROJECTED COST ESTIMATE FOR NICKEL RECOVERY BY REVERSE OSMOSIS (CLOSED-LOOP) SYSTEM (1972)

Parameter	Toronto installation[a]	Projected scale[b]	Projected scale[c]
Flux rate at 450 psi, gal/(ft^2·day)	10.7	10.7	10.7
Permeation rate, gpd	1,065	3,550	35,500
Nominal reverse osmosis unit capacity, gpd	1,000	3,500	35,000
Installed capital cost[d], $	7,000	9,000	37,000
Amortized capital cost per 1,000 gal permeate, $	6.96	2.68	1.03
Operating and maintenance cost per 1,000 gal permeate[d], $	0.70	3.40	2.05
Total cost per 1,000 gal permeate, $	7.66	6.08	3.08
Total cost per day, $	8.15	21.60	109.30
Recovered value per day as Ni, $	9.46	31.50	315.00
Recovered value per day as total salts, $	16.62	55.30	553.00
Savings in deionized water usage per day, $	0.49	1.65	16.50
Total savings as total salts plus water per day, $	17.11	56.95	569.50
Net savings per day, $	8.96	35.35	460.20
Payback on capital investment	39 months	13 months	4 months

[a] Dragout rate = 15 gpd; evaporation rate = 150 gpd.

[b] Dragout rate = 50 gpd; evaporation rate = 500 gpd.

[c] Dragout rate = 500 gpd; evaporation rate = 5,000 gpd.

[d] Capital and maintenance costs can vary widely depending on the design of the unit.

Source: Golomb, A. An Example of Economic Plating Waste Treatment by Reverse Osmosis. In: Proc., 6th International Water Pollution Research Conf., June 18-23, 1973. Reprinted by permission.

McNulty et al.[76] conducted field tests on reverse osmosis treatment of copper cyanide rinse waters and estimated the operating cost for a closed-loop system. These estimates have been revised by TVA to correct an arithmetic error and are presented in Table 38. The total operating cost is calculated to be $2.89/day. The credit realized from the chemicals recovery is shown in Table 39, which indicates total credits of $2.65/shift. These figures show that the operating cost is almost entirely offset by the credits resulting from closed-loop operation.

In applying metal plating industry experience to boiler cleaning wastes, several key differences should be kept in mind. The metal plating industry can often reuse the concentrate as is, and take credit for chemicals saved. Concentrated boiler cleaning waste appears to have no ready market. Also, boiler cleanings occur only once every one to five years, thus large storage areas are necessary if treatment facilities are not to be left idle much of the time.

TABLE 37

TABLE 37. OPERATING AND MAINTENANCE COSTS PER 1000 GALLONS OF PERMEATE FOR NICKEL RECOVERY BY REVERSE OSMOSIS (CLOSED-LOOP) SYSTEM (1972)

Item	Dragout rate 15 gpd	 50 gpd	 500 gpd
Membrane replacement	$0.50	$0.50	$0.50
Power	0.10	0.10	0.10
Labor	Nil	2.70	1.35
Materials	0.10	0.10	0.10
Totals	$0.70	$3.40	$2.05

Source: Golomb, A. An example of Economic Plating Waste Treatment by Reverse Osmosis. In Proc., 6th International Water Pollution Research Conf., June 18-23, 1973. Reprinted by permission.

TABLE 38. BREAKDOWN OF OPERATING COSTS FOR NEW ENGLAND PLATING (1977)

Power

Major power requirement is for the high pressure pump (at 50% efficiency)

$$\frac{(2.67\ \text{gal})}{\text{min}} \cdot \frac{(400\ \text{lb})}{\text{in.}^3} \cdot \frac{(231\ \text{in.}^3)}{\text{gal}} \cdot \frac{\text{ft}}{(12\ \text{in.})} \cdot \frac{(\text{hp-s})}{(550\ \text{ft-lb})} \cdot \frac{\text{min}}{(60\ \text{s})} \cdot \frac{1}{(0.5)} = 1.25\ \text{hp}$$

$$(1.25) \cdot \left(0.746\ \frac{\text{kW}}{\text{hp}}\right) \cdot \frac{(8\ \text{hr})}{\text{shift}} \cdot \frac{(\$.036)}{\text{kWh}} = \frac{\$0.27}{\text{shift}}$$

Module Replacement

$$\frac{\$720}{\text{module}} \cdot \frac{1\ \text{module}}{500\ \text{days}} = \frac{\$1.44}{\text{day}}$$

Maintenance costs (5% of capital investment per year)

$$\frac{.05}{\text{year}} \cdot \frac{\$8500\ \text{capital cost}}{365\ \text{days/year}} = \frac{\$1.16}{\text{day}}$$

Deionized water (at \$2.00 per 1000 gal)

$$\frac{(0.023\ \text{gal DI water})}{\text{min}} \cdot \frac{(8\ \text{hr})}{\text{shift}} \cdot \frac{(60\ \text{min})}{\text{hr}} \cdot \frac{\$2.00}{1000\ \text{gal}} = \frac{\$0.022}{\text{shift}}$$

TOTAL COST PER DAY

One shift per day $\$0.27 + 1.44 + 1.16 + 0.02 = \$2.89/\text{day}$

Three shifts $(0.27 + 0.02) \cdot 3 + 1.44 + 1.16 = \$3.47/\text{day}$

COST PER 1000 GAL

One shift per day $\frac{\$2.89}{\text{shift}} \cdot \frac{1\ \text{min}}{2\ \text{gal}} \cdot \frac{1\ \text{shift}}{480\ \text{min}} \cdot \frac{1000\ \text{gal}}{1000\ \text{gal}} = \frac{\$3.01}{1000\ \text{gal}}$

Three shifts per day $\frac{\$3.47}{\text{day}} \cdot \frac{1\ \text{min}}{2\ \text{gal}} \cdot \frac{1\ \text{day}}{1440\ \text{min}} \cdot \frac{1000\ \text{gal}}{1000\ \text{gal}} = \frac{\$1.20}{1000\ \text{gal}}$

This table is based on the work of K. J. McNulty, R. L. Goldsmith, A. Gollan, S. Hossain, and D. Grant. Reverse Osmosis Field Test: Treatment of Copper Cyanide Rinse Waters. EPA-600/2-77-170, August 1977. Several errors in the original have been corrected, and the labels have been clarified.

TABLE 39. CREDITS REALIZED FOR REVERSE OSMOSIS OPERATION AT NEW ENGLAND PLATING

Value of Recovered Plating Solution (at $1.83/gal)

Loss rate without reverse osmosis system = 0.0013 gal/min.
Recovery rate with reverse osmosis system = 99.96%.

$$\frac{\$1.83}{\text{gal}} \cdot \frac{(0.0013\ \text{gal})}{\text{min}} \cdot (0.9996) \cdot \frac{(480\ \text{min})}{\text{shift}} = \frac{\$1.14}{\text{shift}}$$

Water and Sewer Credits

$$\frac{62\ \text{gal}}{\text{shift}} \cdot \frac{\$0.50}{1000\ \text{gal}} = \frac{\$0.03}{\text{shift}}$$

Chemical Treatment Credits

$$\frac{(0.0013\ \text{gal})}{\text{min}} \cdot \frac{(480\ \text{min})}{\text{shift}} \cdot \frac{(8.9\ \text{oz CuCN})}{\text{gal}} \cdot \frac{(1\ \text{lb})}{16\ \text{oz}} = \frac{0.35\ \text{lb CuCn}}{\text{shift}}\ \text{to treatment}$$

$$\frac{(0.35\ \text{lb CuCN})}{\text{shift}} \cdot \frac{\$0.22}{\text{lb NaOH}} \cdot \frac{1\ \text{lb NaOH}}{1\ \text{lb CuCN}} + \frac{\$0.50}{\text{lb Cl}_2} \cdot \frac{8\ \text{lb Cl}_2}{1\ \text{lb CuCN}} = \frac{\$1.48}{\text{shift}}$$

Total Credits = $2.65/shift

Adapted from: McNulty, K. J., R. L. Goldsmith, A. Gollan, S. Hossain, and D. Grant. Reverse Osmosis Field Test: Treatment of Copper Cyanide Rinse Waters. EPA-600/2-77-170, August 1977.

RECOMMENDATIONS

Reverse osmosis can be used to remove residual heavy metals from chemical cleaning wastes after the bulk has been removed by pH adjustment and precipitation. The design and optimization of such a system will require additional analyses and extensive pilot plant work.

If boiler cleaning wastes were treated at a central facility serving a large number of plants, this would allow for better utilization of treatment facilities. After pH adjustment, precipitation and reverse osmosis, treated water could perhaps be reused to makeup fresh cleaning solutions. A large facility of this type may also be able to market precipitated metals for reuse.

More research is needed to perfect conventional methods of treatment. These would include the use of one or more of the following processes: pH adjustment, aeration, adsorption, chemical precipitation coagulation, settling, or filtration.

SECTION 12

WET SULFUR DIOXIDE SCRUBBER WASTES

CHARACTERISTICS OF WASTEWATER

A study by TVA[25] indicated that the water requirements in a typical closed-loop nonregenerable scrubber system are about 2500 gpm (9463 ℓ/min) per thousand-MW capacity to replace water lost through evaporation and sludge disposal and in washing the mist eliminator to remove accumulated solids. Types of wastewater that might be discharged from nonregenerable scrubber systems include washwater from the mist eliminator, moisture included in the sludge, and occasional bleedoff from the recirculating system. Water is lost to sludge disposal at a rate of about 0.3×10^6 gal (1.1×10^6 L) per day for each percent sulfur in the coal for each thousand-MW capacity of the power plant.[77] Periodic bleeding from the closed-loop scrubber system may be necessary to avoid scaling from the buildup of dissolved solids and to discharge excess water that may occur as a result of changes in operating conditions or system repairs.

The Aerospace Corporation characterized and assessed scrubber liquor discharges from four different closed-loop nonregenerable scrubber systems: pH--3.04 to 10.7; lead--0.01 to 0.4 mg/ℓ; mercury--0.0004 to 0.07 mg/ℓ; selenium--<0.001 to 2.2 mg/ℓ; chloride--420 to 4800 mg/ℓ; sulfate--720 to 10,000 mg/ℓ; arsenic--<0.004 to 0.3 mg/ℓ; boron--8 to 46 mg/ℓ; cadmium--0.004 to 0.11 mg/ℓ; chromium--0.01 to 0.5 mg/ℓ; iron--0.02 to 8.1 mg/ℓ; manganese--0.09 to 2.5 mg/ℓ; and silver--0.005 to 0.6 mg/ℓ.[77]

Mist eliminator wash water, as observed during pilot plant studies at TVA, is generally acidic, with a pH of less than 3, and has relatively high concentrations of iron (0.07 to 13 mg/ℓ) and sulfate (700 to 1200 mg/ℓ).[78]

Regenerable desulfurization scrubber systems often require a particulate scrubber to remove chlorides and fly ash from the flue gas. In addition, the particulate scrubber removes up to half of the SO_3 and between 5 to 20 percent of the SO_2 in the flue gas. Particulate scrubber water is recirculated, but blowdown is necessary to maintain a mass balance in the system. Blowdown from this system is typically high in chlorides and sulfates and very low in pH.

There are many proposed flue gas desulfurization systems, each with its own characteristic wastes. It is beyond the scope of this report to characterize them each in detail.

ALTERNATE TREATMENTS

In general, scrubber liquors become unsuitable for reuse because of high scaling potentials, high dissolved solids (particularly chlorides), or low pH. Of these, membrane technologies are suited to control of dissolved solids but not to alleviating scaling or pH problems. Control of pH and scaling is a necessary prerequisite to either reverse osmosis or electrodialysis.

If membrane technologies are used for dissolved solids control, this will impact the choice of bases for pH adjustment to a neutral value, since the use of lime or limestone would lead to membrane scaling. For equivalent neutralization, lime is cheaper than caustic or soda ash by a factor of 5 to 10. This is important since large quantities of acid must be neutralized.

After neutralization, softening and other pretreatments as appropriate, either reverse osmosis or electrodialysis may be used to remove and concentrate dissolved solids for subsequent disposal. Pretreatment needs are discussed in appendix A.

Evaporative brine concentration has advantages over membrane processes in not requiring extensive pretreatment. Vapor compression evaporators marketed by Resources Conservation Corporation reportedly operate routinely on supersaturated solutions without scaling problems.[79]

Electrodialysis has been suggested as a method of regenerating SO_2 scrubber liquor.[23,24,80] Several variations on this method exist, and no attempt is made to evaluate them fully in this report since scrubber technology is a very complex and growing area. In general, an alkaline-sulfate-sulfite solution is split into separate alkaline and sulfuric acid streams. The alkaline stream is then reused to absorb additional sulfur oxides. Sulfuric acid or SO_2 is recovered for other uses. A three-chamber electrodialysis unit is used. Feedwater enters in the center. Cations such as sodium migrate to the cathode compartment, passing through a cation exchange membrane. At the cathode, cations join with hydroxide ions (OH^-) formed by electrolysis of water. Likewise, anions, such as sulfate and sulfite, pass through the anion membrane where they join with hydrogen ions (H^+) produced by the dissociation of water molecules at the anode.

Regenerable concepts such as this produce less waste material than the so-called throwaway systems. However, lime-limestone scrubbers can be designed for zero liquid discharge, although vast quantities of sludge are produced and must be stored.

RECOMMENDATIONS

Reverse osmosis and electrodialysis should be considered as alternatives to evaporators for the removal and concentration of dissolved solids from scrubber loops, giving consideration to the differing pretreatment requirements. Further studies of scrubber systems should be conducted including those using electrodialysis to regenerate the alkaline scrubber solution.

SECTION 13

RADIOACTIVE WASTEWATERS FROM POWER REACTORS

Because the treatment of radioactive liquid wastes is a complex subject, this section will only attempt to introduce the problem, and place special emphasis on applications of membrane technology.

CHARACTERISTICS OF WASTEWATER

There are two primary mechanisms that produce radionuclides in power reactors--fission and activation. Fission of uranium produces a broad spectrum of radionuclides with mass numbers primarily from 72 to 160.[81] These nuclides then decay to other nuclides. All reactors using uranium-235 yield a similar distribution of fission products, but the quantity released to the reactor coolant varies depending on the number of defects in the fuel cladding.

The reactor coolant and any associated additives or impurities can be activated by neutron bombardment in the reactor core. The primary activation product of water is N^{16}, with smaller contributions from C^{14}, N^{13}, N^{17}, O^{19}, and F^{18}. In pressurized water reactors (PWRs), boron is added to the coolant to control the rate of neutron capture, and lithium is added to control pH. Corrosion products also appear in the coolant. Each nuclide produces its own characteristic family of activation products in quantities determined by the nuclide's "cross section," its concentration, and the neutron flux. For a further discussion of neutron activation, see Glasstone and Sesonske.[82]

From the reactor coolant, radionuclides may take several pathways depending on the plant design and operation. Two types of power reactors predominate in the United States--boiling water reactors (BWRs) and pressurized water reactors (PWRs). In BWRs steam for the turbogenerator is produced in the reactor, whereas in PWRs steam is generated in a heat exchanger, which separates the primary reactor coolant from the secondary coolant.

In BWRs the liquid radioactive wastes are customarily grouped in four categories--high-purity, low-purity, chemical, and detergent waste.[27] High-purity wastes include those collected by closed drains from equipment, including pump and valve leakoffs, demineralizer backwash, and ultrasonic resin cleaning. These liquids are normally reused as primary reactor coolant after appropriate treatment. Low-purity wastes consist of valve and pump leaks and other miscellaneous wastes which are collected by open drains, floor drains, or sumps. Chemical wastes are highly concentrated wastes, primarily spent ion exchange regenerants and laboratory wastes. (Ion exchange is typically used for reactor coolant cleanup, condensate cleanup, and treatment of more dilute radioactive wastes. Resin from these systems may be regenerated or thrown away.) Detergent wastes consist of laundry, personal shower, and equipment decontamination wastes. Approved methods of calculating the activities and quantities of these wastes are given in the BWR-GALE code.[27] To these estimates, conservative designers would add factors to enhance reliability and ease of operation.

PWR waste streams are usually categorized somewhat differently.[83,28] Clean wastes, which originate from leaks in the primary coolant systems, are collected by closed drains. After treatment these wastes are suitable for reuse as primary coolant. Dirty wastes are collected from sumps, floor drains, and other open drains. Floor drain wastes from the turbine building are usually segregated from floor drain wastes from the reactor containment building. Chemical wastes originate (as in BWRs) from spent ion exchange regenerant and laboratory wastes. Again, as in BWRs, ion exchange is used for condensate cleanup, reactor coolant cleanup, and treatment of more dilute radioactive wastes. PWR chemical wastes may be treated separately or combined with floor drain and other dirty wastes. Steam generator blowdown is sometimes used (in addition to or in lieu of condensate polishing) to control steam purity while allowing the use of corrosion inhibitors (usually phosphates) in the steam generator. The properties of this waste are functions of condenser in-leakage, primary-to-secondary coolant leakage, and the amount of corrosion inhibitor used. The volumes and activities of PWR radioactive wastes may be estimated by using the PWR-GALE code.[28] These estimates should be tempered by experience.

Comparing waste streams from PWRs and BWRs, there are many similarities but some significant differences. Chemical wastes originate from laboratory wastes and spent ion exchange regenerant in either type of reactor. The amount and activity of spent ion-exchange regenerant depends more on individual plant design than on the type of reactor. Detergent wastes are also common to both reactor types. Superficially, the high-purity waste from BWRs appears similar to clean waste from PWRs; however, the PWR waste is typically higher in activity and generally contains between 10 and 2000 mg/ℓ of boric acid as boron. Also, both the lithium and boron present in the PWR coolant generate tritium by neutron absorption and subsequent alpha decay. Tritium is a long-lived radionuclide which presents special problems. Low-purity wastes from BWRs are similar to the dirty wastes from PWRs, provided that the PWR dirty wastes are not mixed with chemical wastes. However, PWR floor drains from the containment building are likely to be higher in activity than BWR floor drains, whereas the PWR turbine building will be lower in activity.

In treating PWR wastes, boric acid recovery becomes important. Early in the fuel cycle, the PWR primary coolant may contain about 2000 mg/ℓ boric acid (as boron). As reactivity decreases, boric acid is purposely removed from the coolant. Radionuclides are typically removed from the reactor coolant by a mixed-bed demineralizer saturated in borate ions. The effluent boric acid is reconcentrated by evaporation. When the boric acid concentration in the coolant is very low, reconcentration becomes uneconomical; borate is then removed by an ion exchanger in hydroxide form.

Lithium is used in PWR's to control reactor coolant pH. Because lithium-7 is less prone to generate tritium as an activation product, it is used instead of the more common lithium-6 isotope. Unfortunately, lithium-7 is difficult to separate from naturally occurring lithium, which is a mixture of isotopes. Thus, recovery and reuse of lithium-7 is desired.

Although radioactive wastes are closely monitored and well characterized on the basis of their radioactive elements, less is known about the chemical and physical form of these species. This is a handicap in designing efficient waste treatment schemes. Recent studies indicate significant decontamination factors can be attained by ultrafiltration,[22,84] indicating that some of the radioactive species are not carried as dissolved ions but possibly as colloids or adsorbed onto colloids.

Sometimes the nonradioactive constituents of a waste pose significant problems, as when ion exchange resins are fouled by colloids. Also, evaporator performance is often limited by foaming attributed to organics,[83] and condensate demineralizers are often loaded with ions and colloids from in-leakage of cooling water at the condenser.

ALTERNATIVE TREATMENTS

Reverse osmosis can be used as a roughing demineralizer to increase the time between demineralizer regenerations. This lowers the costs of regenerant chemicals or replacement resins. It can also reduce the cost of solid radioactive waste disposal in the form of spent resins and evaporator bottoms. Whether this results in a net savings depends on several factors, including the available methods for disposing of reverse osmosis reject and ion exchange regenerant, the cost of resin and resin disposal, the cost of regenerant chemicals, and the decontamination factors and personal doses associated with each alternative.

In studying the cost of treating steam generator blowdown, Westinghouse (in an unpublished report) found that reverse osmosis would be more economical than nonregenerable ion exchange if the concentration of total dissolved solids in blowdown exceeded about 80 mg/ℓ. After adjusting the Westinghouse numbers to account for site-specific conditions, TVA found the break-even point to be 15 mg/ℓ, largely because evaporators were already available to process the reject water from reverse osmosis.

Using 80 mg/ℓ as a rough guideline and realizing that a plant-by-plant assessment may be necessary, some generalizations about the applicability of reverse osmosis to radioactive waste demineralization can be made. Reverse osmosis is not applicable to the high-purity or clean wastes, which are very low in dissolved materials (other than boric acid). Furthermore, reverse osmosis is not useful in treating the highly concentrated chemical wastes, with osmotic pressures in the neighborhood of 500 psi. Three potential applications for reverse osmosis are steam-generator blowdown, floor drain wastes, and detergent wastes. These wastes can have dissolved solids contents as high as 80 mg/ℓ, although each waste should be evaluated separately.

The ion loading in steam generator blowdown comes primarily from condenser in-leakage and water treatment chemicals. (The radioactivity comes from primary-to-secondary coolant leakage.) Typical blowdown rates are 0.06 percent of the condensate flow for phosphate treatment and 0.45 percent for all-volatile treatment.[28] Although the condensate may have a relatively low level of dissolved material, this material is concentrated into a much smaller blowdown stream. Total dissolved solids in the blowdown can reach fairly high levels during condenser in-leakage, especially for a seawater-cooled plant. Under these circumstances, reverse osmosis becomes very attractive.

Floor drain wastes gather water leaked from various radioactive systems, combined with other leaks and drains originating from uses of cooling water or potable water. Thus, floor drain waste will have characteristics intermediate between reactor coolant and river water, plus miscellaneous materials (both dissolved and suspended) from other sources. Depending on the individual site and predicted water quality, reverse osmosis may be economical in treating these wastes.

For radioactive wastes, reverse osmosis is best known for treating laundry waste. Westinghouse installed a tubular reverse osmosis station at R. E. Ginna Nuclear Plant and documented its performance,[85] resulting in good acceptance of the concept. To prevent calcium phosphate fouling, deionized or softened water is recommended for laundry makeup water. In fact, the reverse osmosis permeate can be recycled for this purpose.

If deionized water is used in the laundry systems, this makes another system somewhat more attractive than reverse osmosis for treating the waste; carbon filtration can be used to remove organics, followed by ion exchange to remove inorganics.

Each system must be thoroughly evaluated before one could definitely conclude that reverse osmosis is the superior solution to the laundry waste problem. In making such comparisons, care should be taken to consider the pretreatment needs of any proposed reverse osmosis system as stated in the Appendix--User's Guide to Reverse Osmosis. Post-treatment required for radioactive waste streams usually includes ion exchange polishing of the permeate and evaporation of the reject. Evaporation is then followed by solidification and storage.

In many radioactive systems, suspended solids are removed by precoat filters or powdered ion exchange resins. When the pressure across these systems drops excessively, the filter-aid or ion exchange resin is wasted, and creates large volumes of solid radioactive wastes. As an alternative, ultrafiltration could be used to remove colloids and suspended solids. Reject streams could be concentrated to low volumes by reject staging or recycle. The Tsuruga Power Station of the Japan Atomic Power Company Ltd.[22] is using this approach to pretreat wastes from equipment drains. Other possible uses may include condensate demineralizers and floor drain wastes.

Ultrafiltration may also be used to improve the performance of radioactive waste evaporators by pretreating wastes to remove organic materials. This approach is currently being investigated by TERA (Teknekron Energy Resource Analysts) Corporation under contract to EPRI.

Electrodialysis has been proposed as a method of treating reactor coolant from PWR's to separate lithium-7 from boric acid.[23] In this process, lithium ions would be attracted to the cathode through a cation selective membrane, then combined with hydroxide ions generated at the cathode by electrolysis of water. Similarly, borate ions would pass through an anion selective membrane to the anode and combine with hydrogen ions. Subsequent chemical treatments would probably be necessary to separate the desired lithium-7 from other alkali and metals. Boric acid concentrate could presumably also be reused, after purification if necessary. Reverse osmosis might be used to purify boric acid since boric acid will pass through membranes, leaving highly ionized species and colloids behind. (This application of reverse osmosis was suggested by Joseph Markind, now with TERA Corporation.)

RECOMMENDATIONS

In planning future nuclear plants, reverse osmosis should be evaluated for roughing demineralizer service in radioactive systems. This evaluation should take into account the problems of waste disposal, the radiation dose commitments, and the operating and maintenance costs associated with each alternative.

Similarly, reverse osmosis should be evaluated for applications to detergent radioactive wastes, and ultrafiltration should be considered for removal of colloids and suspended solids.

The use of reverse osmosis in laundry and roughing demineralizer applications is proven technology, but the existing experience should be better documented. The efficiency of past processes should also be improved.

Ultrafiltration as a pretreatment process should be demonstrated to provide a basis for estimating performance parameters such as removal efficiencies, decontamination factors, volume recovery factors, and required flow-through rates. With the proper information in hand, detailed evaluations can then be made of ultrafiltration as compared with precoat filters.

The proposed method of recovering lithium and boric acid from PWR coolant deserves further study.

A more detailed review of membrane applications to radioactive wastes has been prepared by the Walden Division of Abcor, Inc.[14]

SECTION 14

MISCELLANEOUS WASTES

CHARACTERISTICS OF WASTEWATER

Miscellaneous wastes can be divided into two groups--oily wastes and nonoily wastes. The oily wastes include wastes from floor drains, oil unloading or transfer stations, oil pumping stations, oil storage tank drainage, oil purification system drains, and equipment base drains. The nonoily wastes include water treatment wastes (excluding ion exchange regeneration wastes), laboratory and sampling streams, and cooling tower basin cleanings.[86] Generally, the nonoily wastes consist of moderate amounts of suspended solids and high amounts of dissolved solids, whereas the oily wastes contain suspended solids, dissolved solids, and oil and grease.

ALTERNATIVE TREATMENTS

Markind et al.[87] investigated the use of the reverse osmosis for concentrating waste-soluble oil coolants. They concluded that reverse osmosis can be used to concentrate soluble coolants to give a permeate that can be reused or dumped to sewers. The economics appeared favorable for the reverse osmosis system as compared with a hauling operation or conventional, physicochemical treatment system.

Bansal's laboratory and pilot studies[88] demonstrated that ultrafiltration with temperature- and abrasion-resistant inorganic (by Union Carbide) membranes can treat oily and latex processing solutions and produce a permeate acceptable for reuse or discharge. The waste oil emulsions can be concentrated to 25 percent or higher. The oil can be concentrated further by sulfuric acid treatment, which yields an oil of 70 percent concentration.

Wang *et al.*[89] reviewed the state-of-the-art of alternative commercial techniques for separating emulsified oil from water, which included air flotation, precipitate flotation, adsorption flotation, magnetization, coalescence, chromatography, layer filtration, absorption-adsorption, centrifuge-hydrocyclone, sedimentation, chemical coagulation, heating-evaporation-distillation, crystallization or freezing, biological oxidation, clarification-flotation, and filtration-extraction-filtration. The oil removal efficiencies of these techniques vary from less than 50 percent to greater than 99 percent. Their costs also vary a great deal. The degree of pretreatment needed before ultrafiltration is determined by the feed quality tolerable to ultrafiltration, the product quality required, and the overall costs incurred. In the ultrafiltration process studied by Bansal[88] only free oil and suspended solids had to be removed before ultrafiltration. With a feed oil concentration as high as 55,600 mg/ℓ, permeates of 5 to 14 mg/ℓ oil were obtained, resulting in 99.97 to 99.99 percent oil rejection. This demonstration seems to cover the range of the oil wastes under consideration in the power plant operation and shows the applicability of the ultrafiltration process.

Generally, devices for removing free oils, such as stilling tanks or belt skimmers, or units for removing suspended solids, such as Sweco or basket filters, are needed before ultrafiltration to treat the oily and nonoily miscellaneous wastes. If Union Carbide's inorganic membranes are used, no pH control is required. Without further treatment, the product water from the ultrafiltration modules can be used for ash sluicing, chemical cleaning, and sulfur dioxide scrubbing.

A cost analysis conducted by Bansal[90] indicates that for a 50,000-gpd unit, the operating cost varies from $2.05 to $3.63 per thousand gallons of waste oil in 1975. The first figure is for a recovery of 90 percent and a membrane life of three years, whereas the second figure is for a 95 percent recovery and a membrane life of two years. If the concentrated oil is recovered and used as fuel, a net profit of $1.95 to $4.37 per 1000 gal can be realized.

Markind et al.[87] reported on an economic study of using reverse osmosis for treating waste coolant oils in 1975. All systems were amortized at 15 percent interest for five years. If the concentrate were burned as fuel (credit of $1.00 per 10^6 Btu or $0.003 per gal of feedwater), total costs would be $0.01/gal for a 500-gpd system. The highest cost would result from the disposal of concentrate at $0.06/gal, which would increase the total costs from $0.016/gal for a 100,000-gpd system to $0.09/gal for a 500-gpd system. A competitive physicochemical treatment system would give a cost of $0.0165/gal for a 100,000-gpd system.

Ultrafiltration and chemical methods of removing oil from waste streams were compared in a panel discussion at the 38th International Water Conference.[91] It was agreed that ultrafiltration can be cost effective in treating oils, but that case by case pilot studies are needed since oily wastes are variable and difficult to characterize. Ultrafiltration was said to produce a more consistent effluent quality than chemical treatment and to be less sensitive to operator errors. It was emphasized that pilot studies are necessary to develop cleaning procedures and schedules.

RECOMMENDATIONS

Ultrafiltration is a competitive technology for treating oily wastes. Pilot studies are necessary on a case-by-case basis to determine operating characteristics as a function of cleaning methods, water recovery rates, and waste characteristics.

SECTION 15

INTEGRATED OR COMBINED WASTES

Power plants are complex and generate a variety of differing waste streams. Many different flow patterns have been devised[41,92,34,46] cascading waters and combining streams for treatment. Plants are now operating with cascading water reuse and zero liquid discharge.[93,79]

To permit maximum water reuse, conventional treatments such as softening, pH control, precipitation, and suspended solids removal are used. If dissolved solids control is not used, the only outflows will be through such incidental losses as entrained water in sludge and cooling tower drift. Deliberate removal and concentration of dissolved solids is often desired to control corrosion. In this event, reverse osmosis, electrodialysis, and distillation should each be considered. Distillation is apparently the most expensive but requires less pretreatment. Electrodialysis is apparently the least expensive,[35] but it does not produce water which is comparable in quality to reverse osmosis permeate or evaporator distillate. Both reverse osmosis and electrodialysis suffer from a lack of large-scale experience in this application within the U.S.

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APPENDIX A

USER'S GUIDE TO REVERSE OSMOSIS

For the past several years TVA has been studying possible applications of reverse osmosis and ultrafiltration to power plant waste treatment. In the process, cognizance of equipment and technical literature has been maintained. Potential power plant applications have been discussed with the plant designers and operators. In addition, some hands-on experience has been gained by treating waste samples in TVA pilot facility, which is equipped to test modules manufactured by Abcor, Dow, DuPont, Osmonics, Romicon, UOP-ROGA, UOP-Fluid Sciences, and Union Carbide.

As a result, TVA has developed a proposed user's guide to reverse osmosis. Using this guide, prospective users may avoid the major pitfalls in selecting reverse osmosis units. Normally, the user must first adequately describe the problem (or opportunity) to vendors and then be able to review and evaluate their proposals. Hopefully, this guide provides a comprehensive list of factors which must be considered in this process. Although new membranes are being developed this guide emphasizes commercial cellulose acetate and polyamide membranes. No attempt to address the dynamic membranes formed by zirconium oxide-polyacrilic acid. If there are other important areas that have been glossed over, comments and discussion with interested readers are welcomed by the authors.

Many problems reported for reverse osmosis systems are not intrinsic to the technology but are due to inadequate design of auxiliary equipment. The consumer must share the responsibility for such problems with designers and vendors.

Feedwater and Pretreatment Criteria

Many of the problems reported with reverse osmosis units stem from inadequate pretreatment. Often, design of the pretreatment system is based on an inadequate description of influent water quality. Where surface water is used, care should be taken to project future changes in water quality. In brackish water areas, future development may cause increased water use upstream, thus degrading water quality and quantity. Overuse of groundwater in coastal areas can cause salt water intrusion. Inland, overpumping may cause ground water levels to drop, decreasing water availability. Variations in weather can also affect water supply and quality. Extended droughts result in lower supplies with increased dissolved solids. High suspended solids are frequently associated with flash floods. The destratification (seasonal overturn) of lakes which occurs as temperatures drop each fall can cause major changes in water quality. Information on natural water quality variations is generally available from State and Federal agencies charged with water pollution control and resource conservation, e.g., U.S. Geological Survey, TVA, and EPA. Industrial water and waste streams should be carefully studied to predict the changes in water quality and quantity which occur due to process changes. (This can be the most difficult task in implementing any industrial waste treatment.) Water analyses should include each of the parameters mentioned below under pretreatment requirements. In addition, the concentrations of major ions must be known.

Parameters that may require control through pretreatment include suspended solids, silica, iron, manganese, biofouling, calcium, magnesium, pH, and temperature. Criteria for control of iron, manganese, calcium, and magnesium are fairly clear, although different control processes can be used. Criteria for controlling suspended solids, biofouling, temperature, and pH vary from one membrane manufacturer to another depending on the configuration and the membrane material.

There are several approaches to setting criteria for influent suspended solids, and a good deal of controversy surrounds the issue. As a potential user, it is best to use all of these approaches if possible so that the maximum number of vendors can be considered. One approach is to use the silt density index test. In this test, feed water under a controlled pressure is forced through a .45 μm (Millipore brand) filter for a fixed time period, usually 15 minutes. The percent plugging is then 100% x $(1-T_1/T_2)$, where T_1 and T_2 are the time intervals required to collect 500 mℓ at the beginning and end of the test, respectively. The silt density index is the percent plugging divided by the total test period in minutes. Where the 15-minute test shows less than 45 percent plugging, the silt density index is less than 3, and membrane fouling should not be a problem, although higher silt densities are tolerable in some systems. Another approach is simply to require a cartridge prefilter rated at 5 to 10 μm. While this protects the membranes from plugging, it does not protect the owner from high operational cost incurred from continually replacing these filters. Also, colloidal fouling can be caused by particles smaller than 5 μm. TVA recommends viewing these replaceable filters as an in-situ test of feed water quality similar to the silt density index. Neither test is strictly comparable to the membrane module since no flow is maintained along the filter to carry away concentrate and no ionic strength variations occur. Ionic strength plays a key role in the stability of colloids and fine particulates and is proportional to the concentration of each ion times the square of its charge. In fact, traditional coagulation practice is based, in part, on destabilization of colloids by increasing the ionic strength. The zeta potential test can be used in conjunction with the silt density index. In this test, colloid mobility in an electric field is observed with the aid of a microscope. The net charge on the colloids is inferred from their size and speed. The higher the electric charge, or zeta potential, the more stable the colloid suspension will be, since like charges repel. Where colloids are stable, higher silt density indexes are tolerable. Another measure of colloid stability is the 24-hour settling test recommended by Osmonics. Each of these approaches is valid in the context of the manufacturer's recommendations.

In general, particulate removal criteria for hollow fiber modules are more stringent than for spiral wound. Where pretreatment to meet these stringent requirements is feasible, both membrane configurations should be considered, since the two types are competitively priced. On the other hand, tubular configurations are much higher in cost but are useful where influent particulate removal is impractical or uncertain. In these cases, periodic cleaning is required, either by chemical or mechanical means.

Pilot plant testing of a reverse osmosis unit is always needed when particulate levels cannot be controlled to meet the manufacturer's criteria. Where regular cleaning is necessary, pilot plant work should include developing cleaning methods and schedules and documenting the expected productivity. Where particulate levels are to be controlled by pretreatment, pilot testing of the membrane is not necesary (at least not to predict particulate fouling). Nevertheless, the efficacy of the pretreatment itself should be tested. This may be done on a bench scale by jar tests or preferably on a larger scale. Pretreated water can then be subjected to the usual criteria for particulate fouling. These may include silt density, zeta potential, the 24-hour settling test, and possibly cartridge filtration to determine the required frequency of replacement.

Methods of removing particulates include coagulation and filtration and ultrafiltration. Inline coagulation is often cost effective. Successful coagulation requires careful operation and control which, though not difficult, does require training. Ultrafiltration is an expensive pretreatment which can sometimes be justified on the basis of its high reliability and relative lack of dependence on operator expertise. This may result in fouling of the ultrafiltration membrane to protect the reverse osmosis membrane. The two are about equally expensive on the basis of surface area, but the ultrafiltration membrane will be cheaper in terms of cost per unit of flow. Also, ultrafiltration membranes are available which can tolerate strong chemical cleaning solutions.

Softening can affect particulate fouling in two ways. Lime-soda ash softening will often trap particulates in the floc which forms. On the other hand, ion exchange softening stabilizes colloids by reducing the ionic strength, which can be helpful in preventing fouling.

Criteria for the control of calcium and magnesium scale are well known. Slide rules, charts, and nomographs abound for determining the Langlier Index, (A1, A2)* recognized criterion for $CaCO_3$ scale. In fresh waters, published solubility constants can be used for guidance with adjustments for ionic strength. See, for example, Chapter 28 of Fair, Geyer and Okun, (A3) for a discussion of this procedure and a list of useful solubility constants. Marshall and Slusher (A4) provide an algorithm for determining $CaSO_4$ solubility in salt waters. Many firms have access to comprehensive computer programs for determing the stability of dissolved species under a variety of conditions. Examples in the public domain include WATEQ (A5) and MINEQL (A6). To predict scaling, the reject water characteristics should be estimated based on the feedwater and the volume recovery desired. The worst case concentration at the membrane surface is then estimated based on the vendor's experience. (Usually this is something like 10 percent more concentrated than the bulk reject flow.) The following species should be checked: $CaSO_4$, $CaCO_3$, and $MgOH_2$.

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*Numbers in parenthesis refer to the list of references at the end of this appendix.

Options to consider for control of calcium and magnesium scales include the use of chemical dispersants, lime soda softening, or ion exchange softening. These processes may in turn affect other pretreatment needs. Lime soda softening affects pH, iron, manganese, silica, and particulates. Ion exchange softening will lower the ionic strength and stabilize particulates. This effect is more dramatic than the lowering of ionic strength alone would indicate, since at a given ionic strength divalent ions are 30 times more effective than monovalent in destabilizing colloids. Ion exchange is also capable of removing iron and manganese, although this can sometimes foul the resin. Dispersants such as sodium hexametaphosphate can also control iron and manganese fouling when used in stoichiometric quantities. Where calcium carbonate scaling is the only problem, pH control alone may be adequate.

Silica scaling is still poorly understood, and good predictive criteria have not yet been established. Silica reacts with nearly every cation, and deposits are often amorphous and difficult to characterize. Some vendor guidelines suggest keeping silica below 100 ppm; others recommend higher limits. Silica can be removed by coprecipitating it with magnesium in the lime-soda softening process.

Iron and manganese fouling presents a special problem in that it takes only a few parts per million to foul the membranes, and yet these species are easily controlled by manipulating pH and redox potentials. Metal cleaning wastes in industry present a similar fouling problem. It is necessary to first destabilize the metal hydroxides by aeration and high pH, remove the precipitate, and finally restablize the supernatant by lowering the pH. The need for treatment is again determined by the predicted concentrations at the membrane surface. Remember that small errors in predicting or controlling pH or redox potential can create a significant problem; thus, allowances should be made accordingly. Stability diagrams showing the log of concentration versus pH for a given metal are helpful in understanding and controlling this problem. The use of these diagrams is discussed in more detail in Fair, Geyer, and Okun (A3) and Stumm and Morgan (A7).

In addition to its role in stabilizing or destabilizing cations, pH is important to membrane life. The most common membrane materials, cellulose acetate and polyamide, are subject to accelerated hydrolysis away from the optimal pH of about 5.5. The polyamide material is less sensitive to pH having a useful pH range of about 4 to 12. In comparison, cellulose acetate membranes are useful between a pH of 3 and 8. At the extremes of these ranges, membrane life decreases dramatically. New membrane materials are being developed which operate in other pH ranges.

Certain weakly ionized species, such as carbon dioxide, ammonia, or silica may exhibit pH dependent salt passage. If these species are important, pH adjustment may be tailored to provide optimal rejections.

Both the performance and the life of reverse osmosis membranes are affected by temperature. Generally, the flux or the permeate rate for both the concentrate and permeate need to be defined. The cost of concentrate handling should be evaluated and included in these criteria--especially if concentrate must be evaporated and stored. The value of recovered water and products should be investigated.

If the goal is to produce high quality water, optimal water recovery is determined by the cost of raw water, pretreatment, and possibly brine disposal. Where the goal is to concentrate the brine for reuse or disposal, recovery is usually limited by scale formation or by osmotic pressure increases.

Estimating Membrane Performance

TVA has tested the performance of seven commercial reverse osmosis modules and found each to meet the manufacturer's specifications with the exception of two tubular units. One of these tubular units was a discontinued product, and specifications were not available. As mentioned before, the cost of commercial tubular units prohibits their use unless fouling is to be expected. This being the case, their performance cannot be accurately predicted in any event without field tests.

For the spiral and hollow fiber modules, performance predictions are often possible by making adjustments for variations from the standard test conditions used in the manufacturer's specifications. The solution-diffusion model is used to make these adjustments. A good discussion of this model is provided in J. W. McCutchan's paper, "Membranes Simplified," presented at the Seminar on Membrane Separation Processes at Clemson University in August 1977. It is assumed that water and the various solutes dissolve in the membrane and diffuse through it in response to pressure and concentration gradients. The following equations result:

$$J_1 = A\ (\Delta P - \Delta \Pi)$$

$$J_2 = B\ \Delta C$$

Here J_1 is the water flux, J_2 is the solute flux, ΔP is the pressure difference, $\Delta \Pi$ is the osmotic pressure, and ΔC is the concentration difference--all measured across the membrane. The membrane itself can be characterized by the coefficients A and B. Note that B varies with each solute. Osmotic pressure can be calculated from solute concentrations. A rough estimate is 10 psi per 1,000 ppm dissolved solids. Osmotic pressure can also be inferred from measurements of boiling point elevation or freezing point depression (A8). Sophisticated computer programs are also available which can provide good estimates of osmotic pressure by taking into account ion pairing and ionic strength corrections.

In TVA tests involving two cellulose acetate and two polyamide modules, no significant variation was found in the permeability coefficient "A" as pressure was varied from 50 to 400 psi. Also, "A" varied with temperature in the same manner as the reciprocal of the absolute viscosity of water.

A plausible explanation for the variation in liquid viscosity with temperature relates it to the energy necessary for a molecule to break free of the liquid matrix (A9). Similarly, a water molecule must free itself from the liquid matrix in order to dissolve in the membrane. Thus, the same mechanism may control both of these processes.

Productivity varies in time as a function of fouling, compaction, and hydrolysis. Where pretreatment is inadequate to prevent fouling, experience developed from pilot testing is necessary to determine membrane productivity. Compaction and hydrolysis are better understood, and manufacturers can often provide guidelines for conservatively estimating these losses. Compaction is a function of the pressure and temperature history of the membrane, while hydrolysis is dependent on the temperature and pH history. To predict productivity from standard test conditions, refer to the fundamental equation for water flux:

$$\frac{J_1}{J_1'} = \frac{(\Delta\bar{P}-\Delta\bar{\Pi})}{(\Delta\bar{P}'-\Delta\bar{\Pi}')} ,$$

where the prime denotes the test conditions. The bars indicate average values taken between the feed and reject conditions.

Besides productivity, the other major performance parameter is solute passage, the ratio of solute concentration in the permeate (C_p) to that in the feed (C_f), expressed as a percentage. Rejection, a related parameter, is simply 100 percent minus the solute passage. From the fundamental flux equations, the following equation for solute passage, SP, can be developed.

$$SP = \frac{C_p}{C_f} = \frac{\bar{J}_2/\bar{J}_1}{C_f} = \frac{B\ (\Delta\bar{C})}{A\ (\Delta\bar{P}-\Delta\bar{\Pi})\ C_f} ,$$

To predict solute passage based on tests at other conditions, the following ratio can be used:

$$\frac{SP}{SP'} = \frac{\Delta\bar{C}}{\Delta\bar{C}'} \cdot \frac{(\Delta\bar{P}'-\Delta\bar{\Pi}')}{(\Delta\bar{P}-\Delta\bar{\Pi})} \cdot \frac{C_f'}{Cf} ,$$

The prime again denotes test conditions.

For the major ions found in natural waters, solute passage information is available both in the literature and from the membrane vendors. Weakly ionized solutes, such as ammonia and H_2CO_3, exhibit pH dependent rejection, and the rejections of cations and anions are interdependent. These factors make exact predictions difficult. Nevertheless, where a membrane exhibits high rejections of NaCl, rejections of other inorganic ions are generally as good or better. The imprecision is usually tolerable. Where extremely high product quality is desired, ion exchange polishing is used. Since the loading to the ion exchanges is low, this is not a costly addition to the process.

Solute passage prediction is generally difficult for weakly ionized inorganics and small organic molecules. If these solutes are important, pilot testing is generally necessary.

TVA was interested in developing rejection data on trace metals. Tests were run on a mixture of metal perchlorates to study their relative salt passage. The trends in these data are not consistent among the membranes tested, nor are they entirely consistent with similar data reported in the literature. Nevertheless, the TVA results may be useful to others, they are shown in Table A1.

Very few reverse osmosis installations are expected to fail because of poor performance predictions, especially where pretreatment is adequate to prevent fouling and the solute rejections have been studied.

Auxiliary Equipment

Many problems have occurred because ot poor auxiliary hardware. DSS Engineers, Incorporated, in a study for the Office of Water Research and Technology (A10), has reviewed 11 commercial desalting plants, including 7 reverse osmosis plants. Anyone purchasing a reverse osmosis system should review their report to identify the potential problems. One of the most common problems was the failure of acid addition systems.

The corrosion resistance of metals, especially those in contact with the liquid, should be stressed in the specifications and should be checked during the bid evaluations and construction. This is not a simple matter. DDS reports that "Corrosion of copper alloys, stainless steels, aluminum, cast iron, and carbon steels has occurred in raw water service at one plant or another. No universally applicable set of materials selections seems possible because of the great variety of raw water constituents and concentrations encountered." Incidentally, corrosion of steel will generally cause membrane fouling downstream. Plastic pipe is corrosion resistant, but is subject to cracking from mechanical stresses due to vibration. Differences in thermal expansion can also cause mechanical stresses where plastic and metal are joined.

Maintenance requirements should be assessed to ensure availability of service and spare parts.

Other mechanical features should be checked. TVA had considerable problems which were solved before obtaining suitable pilot plant operation. These included a piston pump which was not matched to its load, a check valve installed backwards, a faulty solenoid, and a few common fittings mixed in with stainless steel. Problems of this type should be less common on production systems.

Table A1

REJECTION OF METAL PERCHLORATE ON VARIOUS
COMMERCIALLY AVAILABLE MEMBRANES

Ion Membrane	Dow Hollow-Fiber (CTA[a])	DuPont Spiral-Wound[c] (Polyamide)	ROGA Spiral-Wound (CTA[a])	UOP Tubular (CA[b])	Osmonics Spiral-Wound (CA[b])
Mg^{+2}	94.2	84.0	88.9	91.7	92.0
Ca^{+2}	97.2	84.6	84.1	89.9	89.4
Sr^{+2}	83.7	87.3	79.2	88.8	87.5
Ba^{+2}	92.2	98.1	82.8	94.6	93.1
As^{+3}	90.7	88.8	90.7	93.1	91.9
Cd^{+2}	95.4	91.3	85.2	95.9	94.5
Cr^{+6}	97.3	86.4	92.6	96.2	96.0
Cu^{+2}	94.7	82.2	92.6	96.9	96.8
Pb^{+2}	>93.8	>92.3	>92.9	>95.0	>91.4
Mn^{+2}	95.4	90.5	87.5	95.3	94.2
Ni^{+2}	94.9	89.0	83.7	95.7	94.9
Se^{+4}	98.4	81.1	92.2	97.2	98.7
Zn^{+2}	95.0	90.0	87.7	95.2	94.3
Li^{+1}	92.8	69.2	77.6	87.0	77.3
K^{+1}	85.0	81.8	62.5	76.7	66.7
Na^{+1}	87.0	72.7	68.2	76.2	52.6
BO_3^{-3}	28.6	65.5	36.4	68.8	41.7

[a] CTA = Cellulose Triacetate

[b] CA = Cellulose Acetate

[c] This module is not commercially available; however, the membrane material is similar to that in the B-9 hollow-fiber module

[d] Lead (Pb) concentrations in the permeate were below the minimum detectable amount.

Operating Condition

Temperature (°C): 20
Pressure (psig): Dow Hollow-Fiber, 158; DuPont Spiral-Wound, 375; Roga Spiral-Wound, 378; UOP Tubular, 373; Osmonic Spiral-Wound, 378.
Feed Concentration (mg/ℓ): Mg, 25; Ca, 100; Sr, 2.5; Pb, 15; As, 0.15; Cd, 2.5; Cr, 1.0; Cu, 10; Pb, 0.15; Mn, 2.5; Ni, 12.5; Se, 0.5; Zn, 2.5; Li, 2.5; K, 25; Na, 25; B, 10.
pH of solution: 4.8

Conclusion

While reverse osmosis systems design is not an exact science, certain classes of problems can be handled in a straightforward manner. This includes processing solutions of inorganic ions to concentrate or purify, providing that adequate pretreatment is available. Pilot testing of the pretreatment step is advisable, but pilot testing of the reverse osmosis system is not generally necessary. Exceptions include situations where adequate pretreatment is not practical and where organic solutes or weakly ionized species are important.

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APPENDIX B

MEMBRANE SEPARATION OF TOXIC SUBSTANCES IN WASTEWATER

INTRODUCTION

The release of toxic and potential toxic compounds to the environment in industrial wastewaters has created the need to seek a scientific but manageable approach to the identification and control of these chemicals. A major problem in the development of suitable treatment technologies for toxic pollutants is the large number of compounds to be addressed and the vast number of combinations of these substances which may be found in any given waste stream. With the present emphasis on control of specific compounds, the 129 priority pollutants were chosen for assessment of their treatment technologies. These 129 priority pollutants can be classified into 10 groups (B1)*, as shown in Table B1**. This study is concerned with the potential of membrane technology for controlling priority pollutants.

REVERSE OSMOSIS

Separation Mechanism

Reverse osmosis separation is the combined result of preferential sorption of solvent or solute at the membrane-solution interface and the flow of the interfacial fluid through the pores on the membrane surface. Both the porous structure and the chemical nature of the membrane surface together determine the solute and solvent flux through the membrane. This flux is a function of the magnitude of preferential sorption; the effective thickness of the membrane; the size, number, and distribution of pores on the membrane surface; and the operating pressure, temperature, and flow conditions in the apparatus.

The mechanism for inorganic rejection differs somewhat from the mechanism for organic rejection. Theories for reverse osmosis separation of inorganic ions in aqueous solution were proposed on the basis of electrostatic repulsions of ions at the membrane-solution interface (B2-B4). Inorganic salt rejection occurs because the inorganic ions are repelled from the surface of the membrane materials that have a low dielectric with the higher-valence ions being repelled a greater distance. Consequently, the water is absorbed by the membrane surface. The pressure membrane surface. The pressure exerted on the feed solution forces the flow of pure water through the pore if the pore in the membrane is the correct size (twice the pure water layer). The inorganic salts are kept in the concentrated solution.

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*Numbers in parenthesis refer to the list of references at the end of this appendix.

**Because of the large number of tables in this appendix, figures and tables are placed after the text.

Organic rejection is based on the polar and sieve mechanisms. The steric effect is determined by the size and shape of the organic molecule. For example, the approximate size of the pores in a cellulose acetate membrane with 97 percent NaCl rejection is 20 angstroms (2 nanometers). Usually, such a membrane will reject substantially all the organics with a molecular weight above 200 and will reject a percentage of those having a molecular weight between 100 and 200, depending on the shape of the organic molecule. Polyamide and NS-100 membranes may have a smaller pore size than cellulose acetate membranes. The polar effect relevant to reverse osmosis separation, particularly for cellulose acetate membranes, is the acidity (or the proton-donating characteristic) or the basicity (or the proton-accepting characteristic) of the molecule concerned. A quantitative measure of this polar effect is given by either the hydrogen bonding ability or the dissociations constant of the solute. When the acidity of the organic is less than that of pure water, the latter is preferentially sorbed, and positive organic separations are obtainable. When the acidity of the organic is more than that of water, the organic is preferentially sorbed at the membrane-solution interface, and organic separation can be positive, negative, or zero, depending on experimental conditions.

Rejection of Organics

Tables B2 to B5 screen several hundred rejections reported in 18 publications (B5-B22). These tables include data on several varieties of the cellulose acetate membrane, a cellulose acetate butyrate membrane, four varieties of NS-100 membrane, and a duPont polyamide membrane. Much of the information was tabulated by Cabasso, et al. (B23).

In considering the rejections reported from reverse osmosis experiments, one must bear in mind that experimental procedures for the evaluation of rejection efficiency were in most cases the so-called "short run type," as noted by Matsuura and Sourirajan (B5-B10). The data presented by Chian and Fang (B11) indicate that some organic solutes cause inherent membrane properties to change. For example, when a cellulose acetate membrane, which has an initial salt rejection of 97.3 percent (5000 ppm NaCl at 102 atm), was run in a series of short-term experiments while several solutes were measured one after the other. After seven solutes were measured in a row (1000 ppm each of ethanol, i-propanol, acetic acid, formaldehyde, acetone, ethyl ether, glycerol), the salt (NaCl) rejection of the membrane was reduced to 90.1 percent. Several reasons are possible for this decline in the rejection properties of a membrane.

Factors causing reduced rejection may include plasticization of the membrane by absorbed organic solutes that were not flushed out of the membrane. This example was raised to point out that rejection data from the short-term experiments do not necessarily project the precise conditions of organic concentration. However, polyamide membranes did not show such rejection decreases. During organic concentration, the membrane is exposed to several solutes for a relatively longer period of time, and changes in the membrane's inherent rejection properties may result.

The mechanism by which a membrane rejects the passage of certain solutes while permitting water transport is still a matter of great controversy in the cited literature. Nevertheless, some conclusions can be drawn from the data in these tables.

Cellulose Acetate Membranes--

The rejection by membranes prepared from cellulose acetate is highly dependent on the method by which the membrane is prepared and on the degree of acetylation of the starting polymer (B24, B25). In general, a correlation exists between the ability of the solute to form hydrogen bonds with water and the ability of the solute to form bonds with membrane. Dissociated solutes, polyhydric alcohols, and the paraffins are strongly rejected by the membranes. Rejections of phenols in their undissociated state is extremely low; the same characteristic is observed with other organics capable of ionization (Figure B1).

Rejection of organics increases with an increase in the degree of branching and in the number of carbon atoms for compounds having the same functional groups. However, some exceptions to this statement are known, as illustrated in Figure B2, which shows a decrease in rejection of dicarboxylic acids with increasing carbon number. The mechanism of permeability of organic solutes through the membrane probably involves several parameters other than molecular size and the chemical nature of the functional groups.

NS-100 Membranes--

The NS-100 membrane, prepared from an interfacial condensation between an amine and an isocyanate, yields better rejections than do cellulose acetate membranes. Cadotte, et al. (B20) reported the rejections of two versions of this membrane. They classify the preparations of the membrane as a "standard" or a "modified" procedure. The modified procedure yields a more highly cross-linked membrane.

Analysis of the data in Table B4 for NS-100 rejections shows that increasing molecular size (for solutes of the same functional type) leads to better rejections. The higher the cross-link density of membrane surface, the better is the rejection. The nature of the functional group of organic solutes is much less important in governing rejection by the NS-100 membrane than it is for the cellulose acetate membrane.

The excellent rejection of organic solutes by the NS-100 membrane and the wide pH range over which it can operate are attractive features. However, the sensitivity of this material to chlorine (1 ppm or greater leads to reduced rejection) is an impediment to its practical use. The pH stability of the membrane allows operation in both acidic and basic media; this permits alteration in rejection properties of those solutes that act as Lewis bases. The polyurea structure of the membrane is protonated in solutions that have pH values below 10.8. This resembles a Lewis base characteristic of the NS-100 membrane toward higher rejections for amines than for acidic compounds.

Polyamide Membranes--

Chian and Fang (B11) have tested the rejection properties of polyamide membranes toward a variety of solutes. The membranes were provided by duPont's Perma-sep Division as hollow fibers, and flat sheet membranes were supplied by Chemstrand. The rejection of the polyamide is quite similar to that observed for the NS-100 membrane (see Table B5), and it is highly sensitive to the presence of trace levels of chlorine.

In summary, the degree of organic solutes varies with the particular solute-membrane combination. Reverse osmosis treatment of wastewater if generally very effective for removing organic compounds that have molecular weights above 200. Below molecular weight 200, the rejection characteristics are variable, depending on type of membrane used, steric size of the organic molecule, degree of hydrogen bonding that exists, and ionization of the organic molecule.

Molecular weights of organic compounds in the list of priority pollutants range from a low of 50 to a high of over 400. Most of the organic priority pollutants have molecular weights between 100 and 200. The information presented in Tables B2 to B5 indicate that cellulose acetate membranes are not effective for removing low-molecular-weight organics, whereas NS-100 and polyamide membranes will effectively remove a wide class of organic priority pollutants.

Rejection of Heavy Metals

Reverse osmosis shows promise as a purification process for brackish water. Application of reverse osmosis for removing compounds such as calcium, magnesium, and sodium from solution is not pertinent to this topic and will not be discussed here.

Information presented in the literature (B26-B31), indicates that good removal of metallic species in the priority pollutants would probably be achieved with reverse osmosis treatment of wastewater. (See Table B6.) In addition, the bulk of the metal removal would take place in the pretreatment operations, such as clarification or lime softening, required to achieve satisfactory operation of the reverse osmosis process.

ULTRAFILTRATION

Separation Mechanism

The predominate mechanism in ultrafiltration separation is selective sieving through pores. Rejection of an ultrafiltration membrane for a certain substance depends on its molecular shape, size, and flexibility as well as the operating conditions. A useful membrane must be able to separate distinctly at an economical rate. To accomplish this, the ultrafiltration membrane must have a narrow molecular weight cutoff and a high solvent flux at low pressure differentials.

Rejection of Organics

Ultrafiltration membranes generally have nominal molecular weight cutoffs for substances ranging from 500 to 10^6 in molecular weight. The major application for ultrafiltration membranes is for removing colloidal material and large organic molecules in solution. Industrial applications have been successful in treatment of electroplating, pharmaceutical, and laundry wastes; oil-water separation; chemical recovery from waste streams; waste fractionation; and food processing. Since all organic priority pollutants have a molecular weight below 500, ultrafiltration would not be a promising process for removing organic priority pollutants.

Rejection of Heavy Metals

Ultrafiltration will not reject dissolved inorganic salts in solution, and ultrafiltration systems are not concerned with heavy metal removal.

ELECTRODIALYSIS

Separation Mechanism

The principle of electrodialysis separation is the transport of ions through ion-exchange membranes as a result of an electrical driving force. When an electric current passes through the solution compartments and ion-exchange membranes, cations tend to migrate toward the negatively charged electrode (cathode) and anions tend to migrate toward the positively charged electrode (anode). The cations and anions in one set of solution compartments can pass freely through the cation- and anion-exchange membranes that form the walls of this first set of compartments. However, once the cations and anions are in the second set of solution compartments (the alternate compartments), cations are blocked from further transfer because the anion-exchange membranes will not allow their passage. Similarily, anions are blocked from further transfer because they are blocked by cation-exchange membranes. An ion-depleted solution can be withdrawn from the first set of compartments, whereas an ion-enriched solution can be withdrawn from the second set of compartments. The principal limitation of the production rates achievable in electrodialysis units is concentration polarization at the surfaces of the ion-exchange membranes.

Rejection of Organics

Only ionized material can be separated from water by electrodialysis; organics and other un-ionized substances may be concentrated in the demineralized product water. Therefore, the chief function of electrodialysis in the treatment of wastewater is to remove inorganics. In the chemical industry, electrodialysis has been used to recover carboxylic acids (such as acetic, citric, and latic acids) and pulping waste chemicals (such as lignin products) from waste streams (B32). However, electrodialysis is not concerned with removal of organic priority pollutants.

Rejection of Heavy Metals

Desalination of brackish waters is the main commercial use of electrodialysis systems at present. Another area of interest is wastewater demineralization. Electrodialysis has been claimed to be a successful and economical means of removing heavy metals, such as antimony, arsenic, cadmium, chromium, cobalt, copper, manganese, and zinc, from water and wastewaters (B33, B34), but no data are available in support of the claim.

CONCLUSIONS

The results of this assessment, based on published literature, indicate the feasibility of removing priority pollutants from wastewaters by membrane processes. Reverse osmosis is an acceptable process for removing inorganic and organic priority pollutants. Electrodialysis is feasible for removing only inorganic priority pollutants. Ultrafiltration holds no promise for removing priority pollutants from wastewaters.

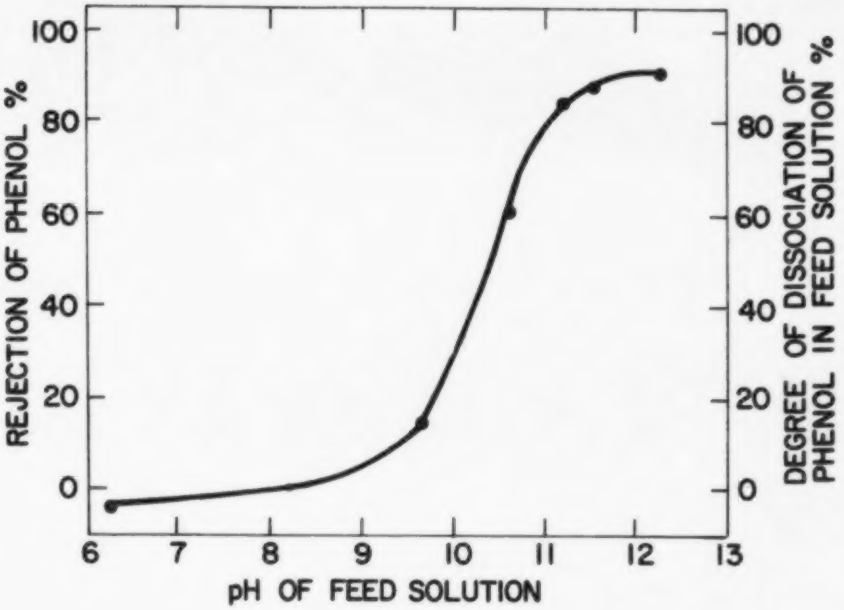

Figure B1. Cellulose acetate membrane rejection of phenol as a function of pH. Source: Matsuura, T., and S. Sourirajan; "Reverse Osmosis Separation of Phenols in Aqueous Solutions Using Porous Cellulose Acetate Membranes." Journal of Applied Polymer Science 16, 2531 (1972). Reprinted by permission.

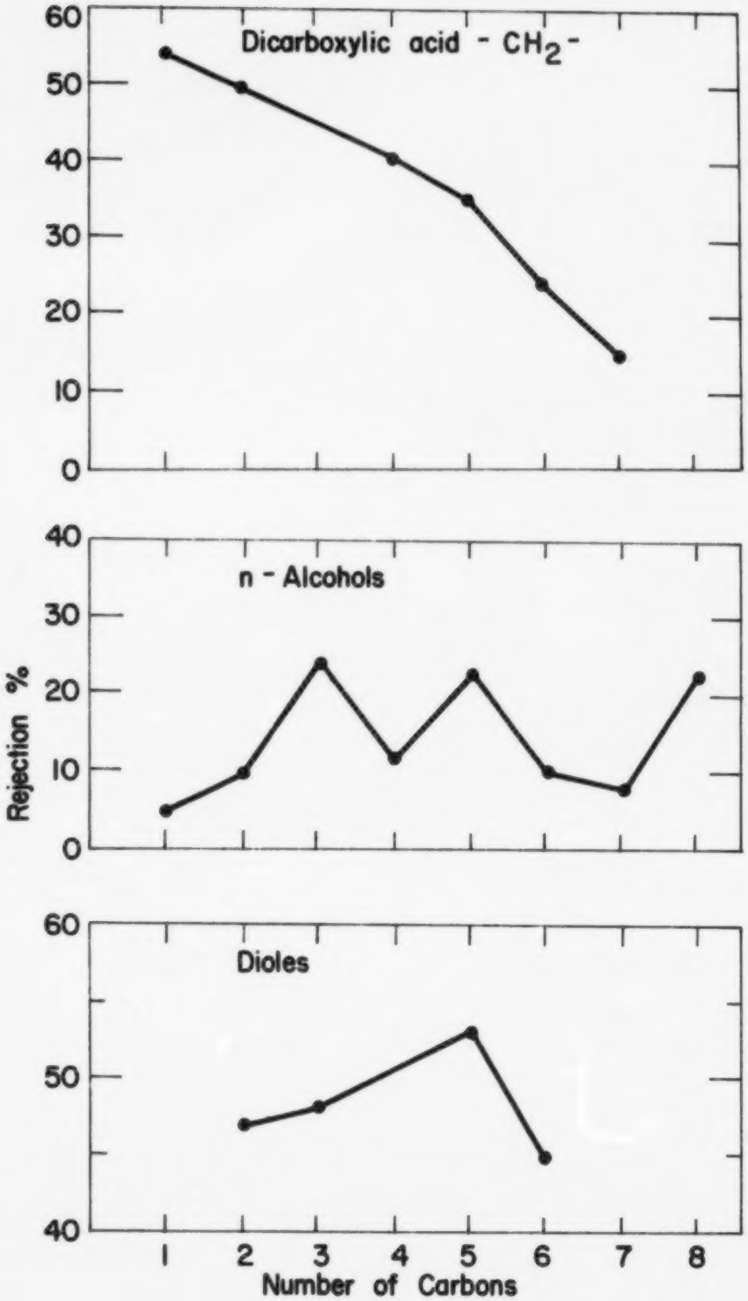

Figure B2. Cellulose acetate membrane rejection of 3 classes of linear alkyl compounds, as a function of the total number of carbons. Source: Cabasso, L., et al., "Evaluation of Semipermeable Membranes for Concentration of Organic Contaminants in Drinking Water." U.S. Environmental Protection Agency, Report No. EPA-670/1-75-001 (1975).

Table B1

LIST OF PRIORITY TOXIC POLLUTANTS

Compound Name		Molecular Weight
I. Pesticides		
1.	Acrolein	56
2.	Aldrin	365
3.	α-BHC	291
4.	β-BHC	291
5.	γ-BHC	291
6.	δ-BHC	291
7.	Chlordane	406
8.	DDD	320
9.	DDE	318
10.	DDT	355
11.	Dieldrin	381
12.	α-Endosulfan	407
13.	β-Endosulfan	407
14.	Endosulfan sulfate	423
15.	Endrin	381
16.	Endrin aldehyde	381
17.	Heptachlor	374
18.	Heptachlor epoxide	389
19.	Isophorone	138
20.	TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin)	332
21.	Toxaphene: $C_{10}H_{10}Cl_6$	343
	$C_{10}H_7Cl_{11}$	517
II. Metals and Inorganics		
1.	Antimony	
2.	Arsenic	
3.	Asbestos	
4.	Beryllium	
5.	Cadmium	
6.	Chromium	
7.	Copper	
8.	Cyanides	
9.	Lead	
10.	Mercury	
11.	Nickle	
12.	Selenium	
13.	Silver	
14.	Thallium	
15.	Zinc	

Table B1. (Continued)

	Compound Name	Molecular Weight
III.	PCB's and Related Compounds	
1.	PCB-1016 (Arochlor 1016)	258
2.	PCB-1221 (Arochlor 1221)	201
3.	PCB-1232 (Arochlor 1232)	232
4.	PCB-1242 (Arochlor 1242)	267
5.	PCB-1248 (Arochlor 1248)	300
6.	PCB-1254 (Arochlor 1254)	328
7.	PCB-1260 (Arochlor 1260)	376
8.	2-Chloronaphthalene	163
IV.	Halogenated Aliphatics	
1.	Methane, bromo- (methyl bromide)	95
2.	Methane, chloro- (methyl chloride)	51
3.	Methane, dichloro- (methylene chloride)	85
4.	Methane, chlorodibromo-	208
5.	Methane, dichlorobromo-	164
6.	Methane, tribromo- (bromoform)	253
7.	Methane, trichloro- (chloroform)	119
8.	Methane, tetrachloro- (carbon tetrachloride)	154
9.	Methane, trichlorofluoro-	137
10.	Methane, dichlorodiflouro-	121
11.	Ethane, chloro-	65
12.	Ethane, 1, 1-dichloro-	99
13.	Ethane, 1, 2-dichloro-	99
14.	Ethane, 1, 1, 1-trichloro-	133
15.	Ethane, 1, 1, 2-trichloro-	133
16.	Ethane, 1, 1, 2, 2-tetrachloro-	168
17.	Ethane, hexachloro-	237
18.	Ethene, chloro- (vinyl chloride)	63
19.	Ethene, 1, 1-dichloro-	97
20.	Ethene, 1, 2-trans-dichloro-	97
21.	Ethene, trichloro-	131
22.	Ethene, tetrachloro-	166
23.	Propene, 1, 2-dichloro-	113
24.	Propene, 1, 3-dichloro-	111
25.	Butadiene, hexachloro-	261
26.	Cyclopentadiene, hexachloro-	273
V.	Ethers	
1.	Ether, bis(chloromethyl)-	115
2.	Ether, bis(2-chloroethyl)-	143
3.	Ether, bis(2-chloroisopropyl)-	171
4.	Ether, 2-chloroethyl vinyl-	107
5.	Ether, 4-bromophenyl phenyl-	249

Table B1. (Continued)

Compound Name	Molecular Weight
6. Ether, 4-chlorophenyl phenyl-	204
7. Bis (2-chloroethoxy) methane	173
VI. Monocyclic Aromatics (excluding phenols, cresols, phthalates)	
1. Benzene	78
2. Benzene, chloro-	113
3. Benzene, 1, 2-dichloro-	147
4. Benzene, 1, 3-dichloro-	147
5. Benzene, 1, 4-dichloro-	147
6. Benzene, 1, 2, 4-trichloro-	182
7. Benzene, hexachloro-	285
8. Benzene, ethyl-	106
9. Benzene, nitro	123
10. Toluene	92
11. Toluene, 2, 4-dinitro-	182
12. Toluene, 2, 6-dinitro-	182
VII. Phenols and Cresols	
1. Phenol	94
2. Phenol, 2-chloro-	129
3. Phenol, 2, 4-dichloro-	163
4. Phenol, 2, 4, 6-trichloro-	198
5. Phenol, pentachloro-	266
6. Phenol, 2-nitro-	139
7. Phenol, 4-nitro-	139
8. Phenol, 2, 4-dinitro-	184
9. Phenol, 2, 4-dimethyl-	122
10. m-Cresol, p-chloro-	143
11. o-Cresol, 4, 6-dinitro-	198
VIII. Phthalate Esters	
1. Phthalate, dimethyl-	194
2. Phthalate, diethyl-	222
3. Phthalate, di-n-butyl	278
4. Phthalate, di-n-octyl-	391
5. Phthalate, bis (2-ethylhexyl)-	391
6. Phthalate, butyl benzyl-	312
IX. Polycyclic Aromatic Hydrocarbons	
1. Acenaphthene	154
2. Acenaphthylene	152

Table B1. (Continued)

Compound Name	Molecular Weight
3. Anthracene	178
4. Benzo (a) anthracene	228
5. Benzo (b) fluoranthene	252
6. Benzo (k) fluoranthene	252
7. Benzo (ghi) perylene	276
8. Benzo (a) pyrene	252
9. Chrysene	228
10. Dibenzo (a, n) anthracene	278
11. Fluoranthene	202
12. Fluorene	166
13. Indeno (1, 2, 3-cd-)pyrene	276
14. Naphthalene	128
15. Phenanthrene	178
16. Pyrene	202
X. Nitrosamines and Other Nitrogen-Containing Compounds	
1. Nitrosamine, dimethyl- (DMN)	74
2. Nitrosamine, diphenyl-	198
3. Nitrosamine, di-n-propyl-	130
4. Benzidine	184
5. Benzidine, 3, 3' -dichloro-	253
6. Hydrazine, 1, 2-diphenyl-	184
7. Acrylonitrile	53

Table B2

REJECTION OF ORGANICS BY CELLULOSE ACETATE MEMBRANES

Solute	Molecular Weight	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Alcohols							
Ethyl Alcohol	46.1	100	4.6	17.0	10		B5
		1000	0.6	40.8	24		B11
		"	1.0	"	13	5.42	B11
		"	0.6	102	37	"	B11
		"	1.0	"	18		B11
n-Propanol	60.1	100	4.6	17.0	24		B5
i-Propanol	60.1	"	"	"	37		B5
		1000	0.6	40.8	60	5.91	B11
		"	1.0	"	44	"	B11
		"	0.6	102	77	"	B11
		"	1.0	"	52	"	B11
Methanol	32.0	100	4.6	17.0	5		B5
		1000	0.6	40.8	-20	5.77	B11
		"	1.0	"	-8	"	B11
		"	0.6	102	-12	"	B11
		"	1.0	102	-8	"	B11
n-Butyl Alcohol	74.1	100	4.6	17.0	16		B5
i-Butyl Alcohol	74.1	"	"	"	41		B5
s-Butyl Alcohol	74.1	"	"	"	34		B5
t-Butyl Alcohol	74.1	"	"	"	79		B5
3-Pentanol	88.2	"	"	"	40		B5
n-Amyl Alcohol	88.2	"	"	"	23		B5
n-Hexyl Alcohol	102.2	"	"	"	11		B5
Cyclohexanol	100.2	"	"	"	60		B5
n-Heptyl Alcohol	116.2	"	"	"	9		B5
n-Octyl Alcohol	130.2	"	"	"	23		B5
Benzyl Alcohol	108.1	"	"	"	5		B5
Phenethyl Alcohol	122.2	"	"	"	8		B5

Lp = Hydraulic permeability constant (flux water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp $\times10^5$	Pressure atm	Rejection %	pH	Reference
Phenols							
Phenol	94.1	1000	1.0	102.0	-18	6.25	B11
		"	.6	40.8	-6	"	B11
		100	4.6	17.0	1		B5, B7
Substituted Phenols							
Chlorophenol	128.6	"	"	"	22		B7
m-Chlorophenol	128.6	"	"	"	20		B7
p-Chlorophenol	128.6	"	"	"	21		B7
p-Chlorophenol	128.6	128	4.6	17.0	42		B10
		"	"	40.8	20		B10
		"	"	68.0	18		B10
		"	"	102.0	1		B10
Pyrocatechol	110.1	100	"	17.0	2		B5
Resorcinol	110.1	"	"	"	-1		B5
		"	"	"	0		B7
Hydroquinone	110.1	"	"	"	1		B5
		1000	1.0	40.8	-0.63	5.20	B11
		"	0.6	40.8	7.03	"	B11
		"	1.0	102.0	-8.20	"	B11
		"	0.6	"	18.19	"	B11
		100	4.6	17.0	4.0		B7
p-Aminophenol	109.1	"	"	"	27.0		B7
p-Methoxyphenol	124.1	100	4.6	17.0	0		B7
p-Cresol	108.1	"	"	"	2		B7
m-Cresol	108.1	"	"	"	2		B7
2,4 Dichlorophenol	163.0	35	-	120.0	-34		B12
m-Nitrophenol	139.1	100	4.6	17.0	2		B7

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Substituted Phenols (cont.)							
p-Nitrophenol	139.1	-	-	20.4	-10	3.0	B13
		-	-	"	70	8.5	B13
		-	-	27	-13	3.0	B13
		-	-	"	78	8.5	B13
		-	-	41	-21	3.0	B13
		-	-	"	80	8.5	B13
		-	-	55	-28	3.0	B13
		-	-	"	81	8.5	B13
		-	-	68	-37	3.0	B13
		-	-	"	82	8.5	B13
		100	4.6	17.0	0		B7
Polyhydric Alcohols							
D-Sorbitol	182.2	"	"	"	99		B5
Dulcitol	182.2	"	"	"	99		B5
Arabitol	152.2	"	"	"	97		B5
Xylitol	152.2	"	"	"	97		B5
Adonitol	152.2	"	"	"	97		B5
1-Erythritol	122.1	"	"	"	94		B5
Glycerol	92.1	1000	0.6	102.0	98	5.95	B11
		"	1.0	"	85	"	B11
Triethylene Glycol	150.0	-	-	100	37		B17
Propylene Glycol	76.1	100	4.6	17.0	68		B5
cis-and-trans-1,2-Cyclohexanediol	116.2	"	"	102.0	83		B5
trans-1,2-Cyclohexanediol	116.2	"	"	"	86		B5
1,6 Hexanediol	118.2	"	"	"	45		B5
1,5 Pentanediol	104.2	100	4.6	102.0	54		B5
1,3 Propanediol	76.1	"	"	"	48		B5
Dextrose	180.2	940	-	102.0	99.7	7	B12

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Aromatics							
Benzene	78.11	100	4.6	17.0	76		B6
		"	"	3.4	97		B6
		"	"	6.8	89		B6
		"	"	33.8	54		B6
Toluene	92.13	"	"	17.0	73		B6
Cumene	120.19	100	4.6	17.0	80		B6
		"	"	6.8	98		B6
		"	"	33.8	71		B6
		"	"	67.6	53		B6
		"	"	102.0	35		B6
Styrene	104.14	100	4.6	17.0	70		B6
Ethylbenzene	106.16	"	"	"	78		B6
o-Xylene	106.16	"	"	"	86		B6
m-Xylene		"	"	"	84		B6
p-Xylene		"	"	"	85		B6
Propylbenzene	120.19	"	"	"	98		B6
t-Butylbenzene	134.12	"	"	"	99		B6
Cyclic Hydrocarbons							
Cyclopentene	68.11	100	4.6	17.0	60		B6
Cyclohexane	84.16	"	"	"	90		B6
Cycloheptatriene	92.1	100	4.6	17.0	66		B6
Cyclohexene	82.1	"	"	"	65		B6
Cyclopentane	70.1	"	"	"	70		B6
Methyl Cyclopentane	84.2	"	"	"	93		B6

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Hydrocarbons							
1,6 Heptadiyne	92.13	100	4.6	17.0	42		B6
1,6-Heptadiene	96.2	100	4.6	17.0	94		B6
Isopentane	72.2	100	4.6	17.0	87		B6
Isoprene	68.11	"	"	"	52		B6
1-Hexyne	82.14	"	"	"	54		B6
1,5 Hexadiene	82.14	"	"	"	59		B6
1-Heptyne	96.17	100	4.6	17.0	77		B6
4-Methyl-1-pentene	84.16	"	"	"	90		B6
2-Methyl-1-pentene	84.2	100	4.6	17.0	92		B6
1-Hexene	84.16	"	"	"	90		B6
n-Hexane	86.17	"	"	"	99		B6
Monocarboxilic Acids							
Pivalic acid	102.1	100	4.6	17.0	66		B7
i-Butyric acid	88.1	"	"	"	35		B7
Valeric acid	102.1	"	"	"	19		B7
n-Butyric acid	88.1	"	"	"	25		B7
Propionic acid	74.1	"	"	"	24		B7
Acetic acid	60.1	"	"	"	24		B7
		1000	1.0	40.8	10	3.97	B11
		"	0.6	"	18	"	B11
		"	1.0	102.0	18	"	B11
		"	0.6	"	30	"	B11
4-Phenylbutyric acid	164.2	100	4.6	"	22		B7

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Monocarboxilic Acids (cont.)							
3-Phenylpropionic acid	150.2	100	4.6	102.0	18		B7
Phenylacetic acid	136.1	"	"	"	26		B7
		"	"	34.0	29		B13
Benzoic acid	122.1	"	"	17.0	19		B7
Caprylic acid	144.2	"	"	"	19		B7
L-Leucine	131.2	1312	-	40	96	3.6	B18
		"	-	"	98	4.5	B18
		"	-	"	99	5.8	B18
p-Aminobenzoic acid	137.1	137	4.6	17.0	13		B7
		"	-	40	2	4.2	B18
		"	-	"	12	3.2	B18
		"	-	"	59	2.3	B18
		"	-	"	75	1.7	B18
m-Aminobenzoic acid	137.1	137	-	40	57	3.9	B18
		"	-	"	70	3.1	B18
		"	-	"	88	2.4	B18
		"	-	"	90	2.0	B18
		"	-	"	96	1.8	B18
Anicic acid	152.1	100	4.6	17.0	20		B7
m-Toluic	136.1	"	"	"	23		B7
m-Hydroxybenzoic acid	138.1	"	"	"	19		B7
m-Nitrobenzoic acid	167.1	"	"	"	37		B7
o-Nitrobenzoic acid	167.1	"	"	"	76		B7
p-Nitrobenzoic	167.1	100	4.6	17.0	35		B7
o-Chlorobenzoic	156.6	"	"	"	45		B7

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Dicarboxylic Acids							
Oxalic acid	90.0	100	4.6	17.0	94		B8
Malonic	104.1	"	"	"	55		B8
Succinic Acid	118.1	"	"	"	50		B8
Adipic	146.1	"	"	"	41		B8
Pimelic acid	160.2	"	"	"	36		B8
Suberic	174.2	"	"	"	25		B8
Azelaic	188.2	100	4.6	17.0	15		B8
Aldehydes							
Formaldehyde	30.0	1000	0.6	40.8	33	4.64	B11
		"	1.0	"	20	"	B11
		"	0.6	102.0	48	"	B11
		"	1.0	"	30	"	B11
Acetaldehyde	44.1	"	4.6	17.0	60		B9
Propionaldehyde	58.1	"	"	"	75		B9
n-Butylaldehyde	72.1	"	"	"	60		B9
i-Butylaldehyde	72.1	100	"	"	78		B9
Crotonaldehyde	70.1	"	"	"	15		B9
Furfuryl	96.1	100	4.6	17.0	2		B9
Benzaldehyde	106.1	"	"	"	10		B9

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Ketones							
Acetone	58.1	100	4.6	17.0	22		B9
		"	-	102.0	17		B13
			-	100	47		B14
		1000	1.0	40.8	5	5.48	B11
		"	0.6	40.8	23	"	B11
		"	1.0	102.0	6	"	B11
		"	0.6	102.0	30	"	B11
Methyl Ethyl Ketone	72.1	100	4.6	17.0	24		B9
		-	-	163	18		B15
Cyclopentanone	84.1	100	4.6	17.0	26		B9
Cyclohexanone	98.1	"	"	"	39		B9
Diisopropyl Ketone	114.2	"	"	"	67		B9
Diisobutyl Ketone	142.2	"	"	"	59		B9
Benzyl Methyl Ketone	134.2	"	"	"	17		B9
Acetophenone	120.1	"	"	"	17		B9

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Ethers - Noncyclic							
Diethyl ether	74.1	100	4.6	17.0	57		B9
		1000	1.0	40.8	12.5	5.59	B11
		"	0.6	"	30.2	"	B11
		"	1.0	102.0	10	"	B11
		"	0.6	"	24	"	B11
Diisopropyl ether	102.2	100	4.6	17.0	84		B9
Anisole	108.1	"	"	"	51		B9
Ethyl vinyl ether	72.1	"	"	"	55		B9
Phenetole	122.2	"	"	"	46		B9
Methyl benzyl ether	122.2	"	"	"	26		B9
Polyoxyethylene Nonylphenyl ether	661.41	52	3.07	40	83.9		B19
	925.5	100	2.75		59.5		B19
	1409.6	238	2.88		92		B19
Cyclic Ethers							
Tetrahydropyran	86.1	100	4.6	17.0	47		B9
Tetrahydrofuran	72.1	"	"	"	53		B9
1,4 Dioxane	88.1	"	"	"	49		B9
Propylene Oxide	58.1	"	"	"	33		B9
Styrene oxide	120.1	100	4.6	17.0	26		B9
Epichlorohydrin	92.5	"	"	"	18		B9

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Esters							
n-Amyl Acetate	130.2	100	4.6	17.0	50		B9
Methyl n-Butyrate	102.1	"	"	"	44		B9
Ethyl acetate	88.1	"	"	"	45		B9
Methyl acetate	74.1	"	"	"	40		B9
		1000	1.0	40.8	-3.53	5.34	B11
		"	0.6	"	20.7	"	B11
		"	1.0	102.0	11.14	5.38	B11
		"	0.6	"	12.36	"	B11
Methyl benzoate	136.1	100	4.6	17.0	25		B9
Ethyl chloroacetate	122.6	"	"	"	9		B9
Methyl chloroacetate	108.5	"	"	"	13		B9
Vinyl acetate	86.1	"	"	"	3		B9
Methyl acrylate	86.1	"	"	"	35		B9
Methyl methacrylate	100.1	"	"	"	40		B9

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Primary Amines							
Aniline	93.1	100	4.6	17.0	4		B9
		1000	1.0	40.8	-9	6.62	B11
		"	0.6	"	22	"	B11
		"	1.0	102.0	-5	"	B11
		"	0.6	"	17	"	B11
		-	-	34	88	6.4	B13
		-	-	"	9	7.3	B13
		-	-	68	78	6.4	B13
		-	-	"	4	7.5	B13
p-Anisidine	123.2	100	4.6	17.0	4		B9
o-Anisidine	123.2	"	"	"	8		B9
p-Toluidine	107.2	"	"	"	7		B9
m-Toluidine	107.2	"	"	"	7		B9
o-Toluidine	107.2	"	"	"	7		B9
m-Phenylenediamine	108.2	"	"	"	15		B9
o-Phenylenediamine	108.2	"	"	"	14		B9
p-Chloroaniline	127.6	"	"	"	14		B9
o-Chloroaniline	127.6	"	"	"	19		B9
m-Chloroaniline	127.6	"	"	"	21		B9
m-Nitroaniline	138.1	"	"	"	8		B9
Secondary Amines							
Di-n-Butylamine	129.5	100	4.6	17.0	63		B9
Piperidine	85.2	"	"	"	88		B9
Dimethylamine	45.1	"	"	"	16		B9
Diisopropylamine	101	-	-	-	72		B17
N-Methylaniline	107.2	"	"	"	12		B9

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Tertiary Amines							
Triethyl	101.2	100	4.6	17.0	95		B9
Trimethyl	59.1	"	"	"	77		B9
N,N-Dimethylbenzylamine	135.2	"	"	"	56		B9
N,N-Dimethylaniline	121.2	"	"	"	33		B9
Miscellaneous							
Nitromethane	61.0	-	-	34	-6	7.2	B13
		-	-	68	-9	"	B13
Boric Acid	43.8	-	-	34	43	7.0	B13
		-	-	68	67	"	B13
		-	-	34	97	11.0	B13
		-	-	68	97	"	B13
Sodium Oleate	304.5	-	-	100	99.9		B16
Sodium dodecylbenzenesulfonate	349.5	210	1.07	40	99.8		B19
Tetradecylbenzylammonium chloride	704.6	188	4.03	"	93.7		B19
Urea	60	-	-	100	45		B17
		1000	1.0	40	17.56	7.22	B11
		"	0.6	"	38.02	"	B11
		"	1.0	102.0	26.76	"	B11
			0.6	"	24.37		B11
2,4 Dichlorophenoxyacetic acid	221	35	-	102.0	92.8		B12

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B2. (Continued)

Solute	Molecular Weight	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Pesticides							
Aldrin	365	0.95	0.9	41.8	100		B12
Atrazine	216	7.34	0.9	41.8	84.0		B12
Captan	301	4.59	0.9	41.8	98.8		B12
DDE	318	0.46	0.9	41.8	100		B12
DDT	354.5	0.28	0.9	41.8	100		B12
Diazinon	304	3.16	0.9	41.8	98.3		B12
Dieldrin	381	2.14	0.9	41.8	99.9		B12
Heptachlor	373	0.97	0.9	41.8	100		B12
Heptachlor epoxide	389	2.05	0.9	41.8	99.8		B12
Lindane	291	3.38	0.9	41.8	99.5		B12
Malathion	330	7.05	0.9	41.8	99.2		B12
Methylparathion	263	6.09	0.9	41.8	99.6		B12
Parathion	291	4.98	0.9	41.8	99.9		B12
Randox	174	2.18	0.9	41.8	72.0		B12
Trifluralin	335.3	10.53	0.9	41.8	99.7		B12

Lp = Hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B3

REJECTION OF ORGANICS BY CELLULOSE ACETATE BUTYRATE MEMBRANES

Solute	Concentration ppm	Lp $\times 10^5$	Pressure atm	Rejection %	pH	Reference
Methanol	1000	0.2	40.8	-9.09	5.77	B11
	"	"	102.4	1.27	"	B11
Ethanol	"	"	40.8	1.9	5.42	B11
	"	"	102.4	14.43	"	B11
i-Propanol	"	"	40.8	41.04	5.91	B11
	"	"	102.4	57.58	"	B11
Acetic Acid	"	"	40.8	12.33	3.77	B11
	"	"	102.4	26.18	"	B11
Formaldehyde	"	"	40.8	41.05	4.64	B11
	"	"	102.4	50.64	"	B11
Acetone	"	"	40.8	16.60	5.48	B11
	"	"	102.4	6.16	"	B11
Ethyl Ether	"	"	40.8	39.51	5.59	B11
	"	"	102.4	2.01	"	B11
Glycerol	1000	0.2	40.8	90.21	5.97	B11
	"	"	102.4	96.08	"	B11
Hydroquinone	"	"	40.8	30.97	5.20	B11
	"	"	102.4	38.15	"	B11
Phenol	"	"	40.8	10.56	6.25	B11
	"	"	102.4	-12.07	"	B11
Urea	"	"	40.8	8.00	7.72	B11
	"	"	102.4	31.36	"	B11
Aniline	"	"	40.8	25.51	6.62	B11
	"	"	102.4	-5.19	"	B11
Methyl Acetate	"	"	40.8	-25.14	5.38	B11
	"	"	102.4	-10.78	"	B11
Sodium Chloride	5000	"	40.8	99.6	6.64	B11
	"	"	102.4	99.8	"	B11

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B4

REJECTION OF ORGANICS BY NS-100 MEMBRANES

Solute	Membrane Designation	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Methanol	Standard	1000	1.0	54.4	33.2	-	B20
	Modified	"	0.5	"	41.0	-	B20
	52C	"	1.1	40.8	-5.98	5.77	B11
	53J	"	1.3	"	18.06	"	B11
	52C	"	1.1	102	1.41	"	B11
	53J	"	1.3	102	9.87	"	B11
Ethanol	Standard	"	1.0	54.4	79.8	-	B20
	Modified	"	0.5	"	86.7	-	B20
	52C	"	1.1	40.8	64.78	5.42	B11
	53J	"	1.3	"	65.66	"	B11
	52C	"	1.1	102	70.01	"	B11
	53J	"	1.3	"	73.57	"	B11
n-Propanol	Standard	"	1.0	54.4	92.7	-	B20
	Modified	"	0.5	"	93.6	-	B20
Isopropanol	Standard	1000	1.0	54.4	91.4	-	B20
	Modified	"	0.5	"	92.3	-	B20
	52C	"	1.1	40.8	82.01	5.91	B11
	53J	"	1.3	"	85.10	"	B11
	52C	"	1.1	102.0	56.06	"	B11
	53J	"	1.3	"	40.16	"	B11
n-Butanol	Standard	"	1.0	54.4	94.2	-	B20
	Modified	"	0.5	"	96.3	-	B20
n-Pentanol	Standard	"	1.0	54.4	95.2	-	B20
	Modified	"	0.5	"	97.7	-	B20
3-Pentanol	Standard	"	1.0	54.4	97.9	-	B20
	Modified	"	0.5	"	99.4	-	B20
Phenol	52C	"	1.1	40.8	68.57	6.25	B11
	53J	"	1.3	"	55.68	"	B11
	Standard	"	1.0	54.4	84.1	-	B20
	Modified	"	0.5	"	87.1	-	B20
	52C	"	1.1	102.0	70.21	6.25	B11
	53J	1000	1.3	102.0	65.72	6.25	B11

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B4. (Continued)

Solute	Membrane Designation	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
p-Chlorophenol	Standard	1000	1.0	54.4	81.0	-	B20
		"	"	17.0	66	-	B20
		"	"	40.8	79	-	B20
		"	"	68.0	80	-	B20
		"	"	102.0	80	-	B20
	Modified	"	0.5	54.4	83.2	-	B20
Formaldehyde	52C	"	1.1	40.8	37.05	4.64	B11
	53J	"	1.3	"	38.62	"	B11
	Standard	"	1.0	54.4	54.7	-	B20
	Modified	"	0.5	"	70.0	-	B20
	52C	"	1.1	102.0	49.96	4.64	B11
	53J	"	1.3	"	50.55	"	B11
Acetaldehyde	Standard	"	1.0	54.0	75.0		B20
	Modified	"	0.5	"	80.6		B20
Benzaldehyde	Standard	"	1.0	"	87.6		B20
	Modified	"	0.5	"	95.0		B20
Acetone	52C	1000	1.1	40.8	80.44	5.48	B11
	53J	"	1.3	"	76.03	"	B11
	Standard	"	1.0	54.0	93.4		B20
	Modified	"	0.5	"	96.1		B20
	52C	"	1.1	102.0	78.26	5.48	B11
	53J	"	1.3	"	77.32	"	B11
Acetophenone	Standard	500	1.0	54.0	96.7		B20
	Modified	"	0.5	"	98.2		B20
Cyclohexanone	Standard	"	1.0	"	97.3		B20
	Modified	"	0.5	"	98.7		B20
Methyl ethyl ketone	Standard	1000	1.0	"	90.8		B20
	Modified	"	0.5	"	95.5		B20

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B4. (Continued)

Solute	Membrane Designation	Concentration ppm	Lp x10^5	Pressure atm	Rejection %	pH	Reference
Acetic acid	52C	1000	1.1	40.8	68.70	3.77	B11
	53J	"	1.3	"	48.02	"	B11
	Standard	"	1.0	54.0	71.0		B20
	Modified	"	0.5	"	80.3		B20
	52C	1000	1.1	102.0	9.00	3.77	B11
	53J	"	1.3	"	69.86	"	B11
Lactic acid	Standard	"	1.0	54.0	87.6		B20
	Modified	"	0.5	"	89.3		B20
Benzoic acid	Standard	500	1.0	"	66.3		B20
	Modified	"	0.5	"	82.0		B20
Ethylamine	Standard	1000	1.0	"	86.2		B20
	Modified	"	0.5	"	92.8		B20
Triethylamine	Standard	"	1.0	"	99.7		B20
	Modified	"	0.5	"	98.5		B20
Aniline	52C	"	1.1	40.8	31.36	6.62	B11
	53J	"	1.3	"	51.80	"	B11
	Standard	"	1.0	54.0	91.8		B20
	Modified	"	0.5	"	95.9		B20
	52C	"	1.1	102.0	14.99	6.62	B11
	53J	"	1.3	"	31.31	"	B11
Methyl acetate	52C	1000	1.1	40.8	36.37	5.38	B11
	53J	"	1.3	"	28.32	"	B11
	Standard	"	1.0	54.0	89.2		B20
	Modified	"	0.5	"	91.7		B20
	52C	"	1.1	102.0	23.02	5.38	B11
	53J	"	1.3	"	44.62	"	B11
Ethyl acetate	Standard	"	1.0	54.0	95.8		B20
	Modified	"	0.5	"	96.9		B20
Ethyl ether	52C	"	1.1	40.8	90.93	5.59	B11
	53J	"	1.3	"	82.18	"	B11
	52C	"	1.1	102.0	65.62	"	B11
	53J	"	1.3	"	77.09	"	B11

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B4. (Continued)

Solute	Membrane Designation	Concentration ppm	Lp $\times 10^5$	Pressure atm	Rejection %	pH	Reference
Glycerol	52C	1000	1.1	40.8	96.87	5.97	B11
	53J	"	1.3	"	89.15	"	B11
	52C	"	1.1	102.0	96.18	"	B11
	53J	"	1.3	"	91.69	"	B11
Hydroquinone	52C	1000	1.1	40.8	82.23	5.20	B11
	53J	"	1.3	40.8	71.93	5.20	B11
	52C	"	1.1	102.0	86.29	"	B11
	53J	"	1.3	"	77.38	"	B11
Urea	52C	1000	1.1	40.8	64.15	7.72	B11
	53J	"	1.3	"	55.37	"	B11
	52C	"	1.1	102.0	74.32	"	B11
	53J	"	1.3	"	63.38	"	B11
NaCl	53J	5000	1.3	40.8	99.71		B11
	52C	"	1.1	102.0	99.26		B11
	53J	"	1.3	"	99.24		B11
Pesticides							
Aldrin		0.95	1.36	41.8	100		B22
Atrazine		7.34	1.36	41.8	97.8		B22
Captan		4.59	1.36	41.8	100		B22
DDE		0.46	1.36	41.8	100		B22
DDT		0.28	1.36	41.8	100		B22
Diazinon		3.16	1.36	41.8	88.1		B22
Dieldrin		2.14	1.36	41.8	100		B22
Heptachlor		0.97	1.36	41.8	100		B22
Heptachlor epoxide		2.05	1.36	41.8	99.8		B22
Lindane		3.38	1.36	41.8	99.0		B22
Malathion		7.05	1.36	41.8	99.7		B22
Methylparathion		6.09	1.36	41.8	99.6		B22
Parathion		4.98	1.36	41.8	99.8		B22
Randox		2.18	1.36	41.8	98.6		B22
Trifluralin		10.53	1.36	41.8	100		B22

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B5

REJECTION OF ORGANICS BY POLYAMIDE MEMBRANES

Solute	Membrane Type	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Methanol	B-9	536	-	27.2	28.01		B11
	B-9	500-2000	-	-	0		B21
	-	1000	.43	40.8	19.10	5.77	B11
	-	"	"	102.0	5.42	"	B11
Ethanol	B-9	677	-	27.2	36.49		B11
	B-9	500-2000	-	-	28		B21
	-	1000	.43	40.8	57.46	5.42	B11
	-	1000	"	102.0	70.45	"	B11
i-Propanol	B-9	1174	-	27.2	90.05		B11
	B-9	500-2000	-	-	75		B21
	-	1000	.43	40.8	88.97	5.91	B11
	-	"	"	102.0	95.53	"	B11
Acetic acid	B-9	682	-	27.2	31.28		B11
	B-9	500	-	-	40		B21
	-	1000	.43	40.8	70.14	3.77	B11
	-	"	"	102.0	82.21	"	B11
Formaldehyde	B-9	1278	-	27.2	21.19		B11
	-	1000	.43	40.8	52.10	4.64	B11
	-	"	"	102.0	68.61	"	B11
Acetone	B-9	856	-	27.2	52.93		B11
	-	1000	.43	40.8	71.96	5.48	B11
	-	"	.43	102.0	72.24	"	B11
Ethyl ether	B-9	388	-	27.2	57.67		B11
	-	1000	.43	40.8	89.74	5.59	B11
	-	"	"	102.0	91.67	"	B11
Glycerol	B-9	765	-	27.2	87.85		B11
	B-9	500-2000	-	-	90		B21
	-	1000	.43	40.8	88.04	5.97	B11
	-	"	"	102.0	88.14	"	B11

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B5 (continued)

Solute	Membrane Type	Concentration ppm	Lp $x10^5$	Pressure atm	Rejection %	pH	Reference
Hydroquinone	B-9	551	-	27.2	60.49		B11
	-	1000	.43	40.8	84.49	5.20	B11
	-	"	"	102.0	98.61	"	B11
Phenol	B-9	773	-	27.2	44.67		B11
	B-9	500-2000	-	-	55		B21
	-	1000	.43	40.8	80.06	6.25	B11
	-	"	"	102.0	88.72	"	B11
Urea	B-9	1188	-	27.2	34.45		B11
	-	1000	.43	40.8	55.41	7.72	B11
	-	"	"	102.0	89.32	"	B11
Aniline	B-9	440	-	27.2	47.28		B11
	-	1000	.43	40.8	78.08	6.62	B11
	-	"	"	102.0	82.19	"	B11
Methyl Acetate	B-9	370	-	27.2	57.45		B11
	-	1000	.43	40.8	54.31	5.38	B11
	-	"	"	102.0	44.50	"	B11
Sodium chloride	B-9	3850	-	27.2	93.06		B11
	B-9	1500	-	-	90		B21
	-	5000	.43	40.8	99.13	6.64	B11
	-	"	"	102.0	99.58	"	B11

Lp = hydraulic permeability constant (flux of water/differential hydraulic pressure, ml/cm^2 sec atm)

Table B6

REJECTION OF HEAVY METALS BY REVERSE OSMOSIS MEMBRANES

Solute	Membrane Type	Concentration ppm	Pressure atm	Rejection %	pH	Reference
Arsenic	Cellulose acetate	0.15	12	90.7	4.8	*
	Cellulose acetate	0.15	26.5	90.7-93.1	4.8	*
	Polyamide	0.15	26.5	88.8	4.8	*
Boron	Cellulose acetate	0.35	-	38-60	5	B26
	Cellulose acetate	10	12	28.6	4.8	*
	Cellulose acetate	10	26.5	36.4-68.8	4.8	*
	Polyamide	10	26.5	65.5	4.8	*
Barium	Cellulose acetate	9.15	28.2	97.8	-	B31
	Cellulose acetate	15	12	92.2	4.8	*
	Cellulose acetate	15	26.5	82.8-94.6	4.8	*
	Polyamide	15	26.5	98.1	4.8	*
Cadmium	Cellulose acetate	-	-	78-99+	11.5	B27
	Cellulose acetate	1	28.2	98.7-99	-	B31
	Cellulose acetate	2.5	12	95.4	4.8	*
	Cellulose acetate	2.5	26.5	85.2-95.9	4.8	*
	Polymide	2.5	26.5	91.3	4.8	*
Chromium	Cellulose acetate	-	-	86-98	0.9-1.9	B27
	Cellulose acetate	-	-	92.6	2.6	B26
	Cellulose acetate	-	-	52-99	4.4-4.7	B27
	Cellulose acetate	-	-	91-99+	5.5-6.1	B27
	Cellulose acetate	-	-	98.6	7.6	B26
	Cellulose acetate	0.94-1.01	28.6	95-96.9	-	B31
	Cellulose acetate	8.65-9.35	28.2	85.1-93.2	-	B31
	Cellulose acetate	1	12	97.3	4.8	*
	Cellulose acetate	1	26.5	92.6-96.2	4.8	*
	Polyamide	1	26.5	86.4	4.8	*
	NS-100	12.5	41.8	97.6	8	B31
	NS-100	12.5	41.8	91.3	11	B31

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*This study

Table B6. (Continued)

Solute	Membrane Type	Concentration ppm	Pressure atm	Rejection %	pH	Reference
Copper	Cellulose acetate	0.65-0.7	28.2	94.8-97+	-	B31
	Cellulose acetate	6.25-6.5	28.2	99.2-99.6+	-	B31
	Cellulose acetate	10	12	94.7	4.8	*
	Cellulose acetate	10	26.5	92.6-96.9	4.8	*
	Polyamide	10	26.5	82.2	4.8	*
	NS-100	12.5	41.8	99.9	8	B31
	NS-100	12.5	41.8	99.9	11	B31
Iron	Cellulose acetate	6.5	-	98.2	6.7	B30
	NS-100	12.5	41.8	100	8	B31
	NS-100	12.5	41.8	100	11	B31
Lead	Cellulose acetate	0.95-1.1	28.2	97.8-99.5+	-	B31
	Cellulose acetate	4.8-9.3	28.2	97.8-99.9	-	B31
	Cellulose acetate	0.15	12	93.8+	4.8	*
	Cellulose acetate	0.15	26.5	91.4+	4.8	*
	Polyamide	0.15	26.5	92.3+	4.8	*
	NS-100	12.5	41.8	100	8	B31
	NS-100	12.5	41.8	100	11	B31
Manganese	Cellulose acetate	3.8	-	100	6.7	B30
	Cellulose acetate	2.5	12	95.4	4.8	*
	Cellulose acetate	2.5	26.5	87.5-95.3	4.8	*
	Polyamide	2.5	26.5	90.5	4.8	*
Mercury (organic)	Cellulose acetate	100	18	63.2	-	B28
	Cellulose acetate	140	18	66.1	-	B28
Nickel	Cellulose acetate	1000	14.6	99	4-6	B29
	Cellulose acetate	1000	21.4	99.6	4-6	B29
	Cellulose acetate	12.5	26.5	94.9	4.8	*
	Cellulose acetate	12.5	26.5	83.7-95.7	4.8	*
	Polyamide	12.5	26.5	89	4.8	*
	NS-100	12.5	41.8	96.3	8	B31
	NS-100	12.5	41.8	98.8	11	B31

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*This study

Table B6. (Continued)

Solute	Membrane Type	Concentration ppm	Pressure atm	Rejection %	pH	Reference
Selenium	Cellulose acetate	0.5	12	98.4	4.8	*
	Cellulose acetate	0.5	26.5	92.2-98.7	4.8	*
	Polyamide	0.5	26.5	81.1	4.8	*
Strontium	Cellulose acetate	2.5	12	83.7	4.8	*
	Cellulose acetate	2.5	26.5	79.2-88.8	4.8	*
	Polyamide	2.5	26.5	87.3	4.8	*
Zinc	Cellulose acetate	9.4-10	28.2	96.9-98.6	-	B31
	Cellulose acetate	32.8-31.4	28.2	98.8-99.5	-	B31
	Cellulose acetate	2.5	12	95	4.8	*
	Cellulose acetate	2.5	26.5	87.7-95.2	4.8	*
	Polyamide	2.5	26.5	90	4.8	*
	NS-100	12.5	41.8	97.9	8	B31
	NS-100	12.5	41.8	100	11	B31

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*This study

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16. ABSTRACT The report gives results of an examination of three membrane technologies (reverse osmosis, ultrafiltration, and electrodialysis) for wastewater treatment and reuse at electric power generating plants. Recirculating condenser water, ash sluice water, coal pile drainage, boiler blowdown and makeup treatment wastes, chemical cleaning wastes, wet SO2 scrubber wastes, and miscellaneous wastes were studied. Membrane separation of toxic substances in wastewater was also studied. Waste characteristics, applicable regulations, feasible membrane processes, and cost information were analyzed for each waste stream. A user's guide to reverse osmosis was developed and is provided as an appendix. Power plant water treatment with membrane technologies to attain total water reuse and zero effluent discharge is technically feasible. Membrane technologies are not suited to remove materials that are unstable and apt to precipitate as they are concentrated; however, they excel in separating materials not susceptible to conventional wastewater treatment (e.g., very soluble toxics and dissolved solids). Thus membrane technologies complement rather than compete with conventional technologies. For dissolved solids control, membrane technologies are viable alternatives to distillation. Distillation is more costly, but requires less pretreatment than reverse osmosis or electrodialysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Electrodialysis	Pollution Control	13B	
Waste Water	Toxicity	Stationary Sources		06T
Water Treatment	Dissolved Organic	Membrane Separation		
Membranes	Matter	Reverse Osmosis	11G	08H
Electric Power Plants		Ultrafiltration	10B	
Osmosis Filtration	Distillation	Dissolved Solids	07D	13H,07A

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